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"SOLVENTLESS LAMINATION ADHESIVE - A INTROSPECTION"

MAJOR PROJECT DISSERTATION
SUBMITTED TO THE DEPARTMENT OF APPLIED CHEMISTRY,
POLYMER SCIENCE & CHEMICAL TECHNOLOGY
DELHI COLLEGE OF ENGINEERING
DELHI UNIVERSITY
DELHI

BY
SHAILENDRA KUMAR SRIVASTAVA

IN PARTIAL FULFILLMENT OF THE REQUIRMENT FOR
THE DEGREE OF MASTER OF ENGINEERING
IN
POLYMER TECHNOLOGY
SEPTEMBER, 2002

CERTIFICATES

This is to certify that the thesis entitled "SOLVENTLESS LAMINATION ADHESIVE - A INTROSPECTION ", being submitted by Mr. Shailendra Kumar Srivastava to the Delhi College of Engineering, University of Delhi, Delhi, for the Award of Master of Engineering is a record of bonafide research work carried out by him. Mr.Shailendra Kumar srivastava has worked under our guidance and supervision and has fulfilled the requirement for the submission of the Project Report.

The results contained in this Project Report have not been submitted in part or in full, to any other university or institute for the award of any degree or diploma.

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CHAPTER - 1

INTRODUCTION

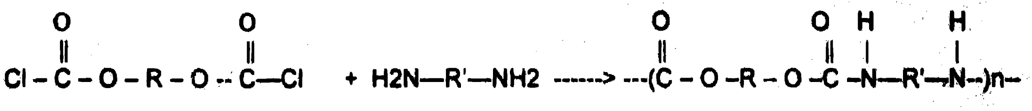
1.1 POLYURETHANE

The name polyurethane was derived from ethylcarbamate known as urethane. The commercial development of polyurethane was actively pursued in Germany from 1930 to present day. It was infact, a vigorous research programme in the laboratories of I.G. Ferbenindustrie and its successor Bayer A.G. which led to the production of rigid and flexible foams, adhesives, coatings, fibers and elastomers (moulding grade) in the late 19th century .Although, DU Pont (USA) and ICI (UK) showed an early interest in this class of polymers, a break through could not be achieved till the flexible foam technology of Bayers was transferred to USA in 1950s. Recently, introduction of reaction injection moulding of polyurethane technology added a new dimension to its development.

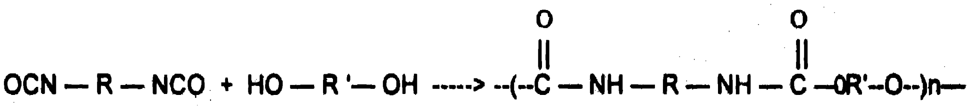
The high potentiality of polyurethane in diversified field of application is due to the flexibility in selecting reactants. The high reactivity of one of the reactants (diisocyanate) with various functional groups resulted in the development of fairly board class of polymers.

1.1.1 Urethane Homopolymers

Urethane homopolymers are associated only with carbamate repeat units. These are prepared by following methods.



$$Cl-\overset{O}{\overset{\|}{C}}-O-R-O-\overset{O}{\overset{\|}{C}}-Cl + H2N-R'-NH2 \longrightarrow -(\overset{O}{\overset{\|}{C}}-O-R-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R'-\overset{H}{\overset{|}{N}}-)_n-$$



$$OCN-R-NCO + HO-R'-OH \longrightarrow -(\overset{O}{\overset{\|}{C}}-NH-R-NH-\overset{O}{\overset{\|}{C}}-OR'-O-)_n-$$

The commercial process of production of polyurethane homopolymer generally involves reaction of diisocyanate with active hydrogen functional group of a compound. Commercially known Polyurethane homopolymer are perlon U, Igamid U , Durathane etc.These polymer are stiff , highly crystalline and their physical properties are similar to polyamide.These polymers lost their commercial significance with introduction of Nylon. In fact, the production of these polymers was discontinued in early 1980s.

1.1.2 Urethane Copolymers

In contrast to urethane homopolymers, copolymers attracted much commercial significance since the early days of 1950s.

This class of polymer has wide range of physical and chemical properties. The Polyurethane block copolymer

Shows more commercial importance than any other class of polyurethane.

1.1.2.1 Urethane Block Copolymer

A block copolymer is defined as polymer comprising of molecules in which there is a linear arrangement of blocks. A block is defined as a portion of a polymer molecule in which monomeric units have at least one constitutional or configurational feature absent from adjacent portion. Block copolymer are often called segmented copolymer. This is due to the fact that these polymers may be considered as composed of two or more polymer molecules attached end to end. Each of these polymeric molecules is called segment of block.

Polyurethane copolymer is composed of two type of segments, hard and soft segments. The soft segments are usually derived from hydroxyl terminated polyethers, polyesters and polyalkyl diol (mol wt. 600 -3000). These segments have the glass transition temperature (temp) below the temperature of use. Therefore, these long flexible segments are in rubbery state at room temperature and are thus called as soft segments. The hydroxyl end of these segments are first reacted with an isocyanate end of a diisocyanate.The isocyanate capped soft segment is then chain extended either with a diamine or diol leading to the formation of block copolymer. The amine and isocyanate derivative part of block copolymer is called hard segments. This segment has glass transition temperature

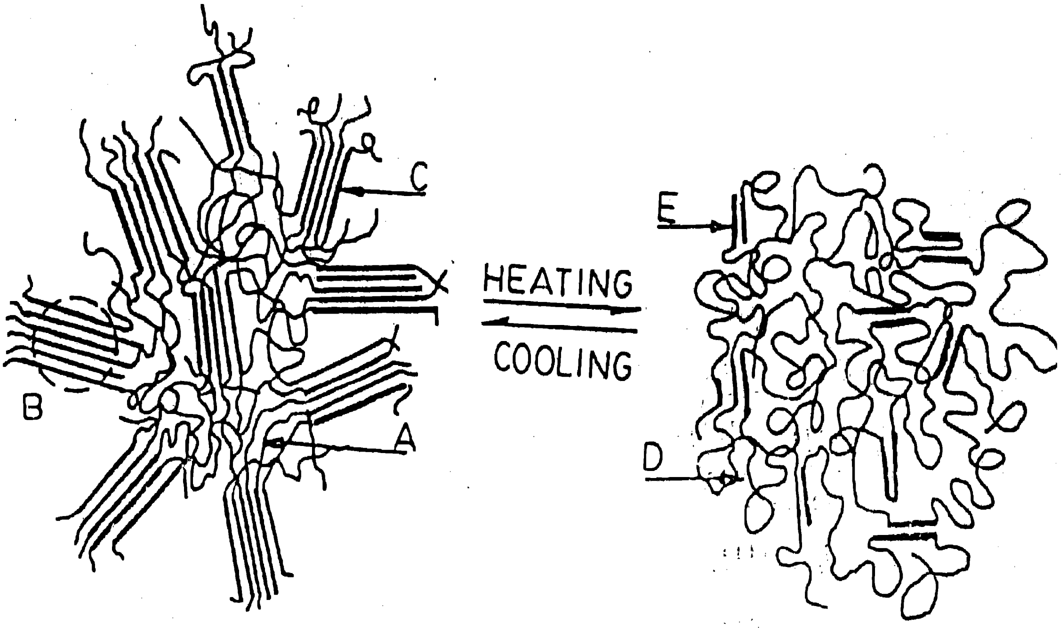


Fig. 1 Morphological model for phase mixing/ remixing. A) Partially extended soft segment B) Hard Segment domain C) Hard segment D) Relaxed soft segment E) Lower -Order Hard -Segment Domain
(Taken from Wilkes, G.L., Emerson, J.A., J. Appl. Phys., 47, 4261, 1976).

above room temperature. It is rigid and glassy at room temperature.

The wide difference of physiochemical properties of hard and soft segments induces phase segregation and microdomain formation. The soft phase generally composed of soft segments with impurities of hard segments. This phase is usually responsible for elastic or rubbery behavior of the material. The hard segments are also called hard domain. These are of various size, shape and distribution. The hard domains are responsible for mechanical properties due to strong dipole interaction and hydrogen bonding .Usually, these domains act as fillers or physical cross links for soft matrix.

The two phase structure of polyuretane is temperature dependant i.e. the two phase structure reverses to single phase on heating. This deformation and reformation of domain structures under different thermal condition is presented schematically in figure 1. Usually, a single phase structure at higher temperature slowely returns to two phase system on cooling. Therfore, polyurethane block copolymer shows different morphology depending on thermal history of material. So by the process of annealing properties of polyurethane can be changed.

1.1.2.2 Annealation of Block Copolyurethane

Annealation is a process of thermal treatement given to a polymer. Annealation of polyurethane copolymer above 200 °C increases crystalline order in the matrix. Annealation below 200 °C does not affect the

micro-crystalline ordered structure but changes the structure of other ordered forms, namely.

(1) Short range order , with domain disruption at temperature around 70 C
(2) Long range order, with domain disruption temperature centered around 120-190 C.
(3) Crystalline order , with melting of micro-crystalline order at about 200 C

The short range and long range order shifts and merges with each other on annealation. The extent of shift depends on temperature and time of annealation. The long range order endotherm, on the other hand, can shift and merge with micro-crystalline melting endotherm. The latter is probable only when hard block of sufficient length is annealed for long time.

Similarly, annealation of polyurethane copolymer above soft segment crystallisation temperature and below the melting point of soft segment results in increase in size of soft segment crystalline structure.

The thermal annealation above the temperature of crystallization of soft segment increases the soft segment glass transition temperature (Tg) because of increase in crystal size. The thermal treatment above Tg of soft segment and below 200 °C decreases hysteresis , permanent set , tensile strength and young's modulus, while, there is an opposite trend with annealation above 200 °C . This difference may be attributed to difference in structural development.

1.1.2.3 Bulk Morphology and Physical Properties

Physical characteristic of polyurethane block copolymer depend on four factors; 1) Composition of domain, 2) Conformation of domain, 3) Distribution of domain and, 4) Degree of segregation.

The physical composition, molecular weight and symmetry of the structure of soft segment, affect the Tg, elongation at break, initial modulus and tensile strength. Increase in soft segment molecular weight and its symmetry at a fixed hard segments length results in decrease in strength and modulus but increase elongation at break due to decrease in cross linking density. A reverse trend is observed with increase in concentration of hard segments or symmetry in structure. A decrease in soft segment length at constant hard segment concentration or decrease in symmetry of structure of hard segment generally lowers mechanical properties and increases glass transition temperature of soft phase, due to mixing of phase. A decrease in the molecular symmetry of the hard segments (using TDI) disturb the phase segregation to the extent that the matrix laminates single phase structure these material generally behaves as homopolymer or random copolymers (maximum random in structure) . However, chemically this material remains block copolymers. Generally this material are used in lower applications (non elastomeric) therefore, it is apparent that bulk morphology plays a dominant role in the end use of the polymer.

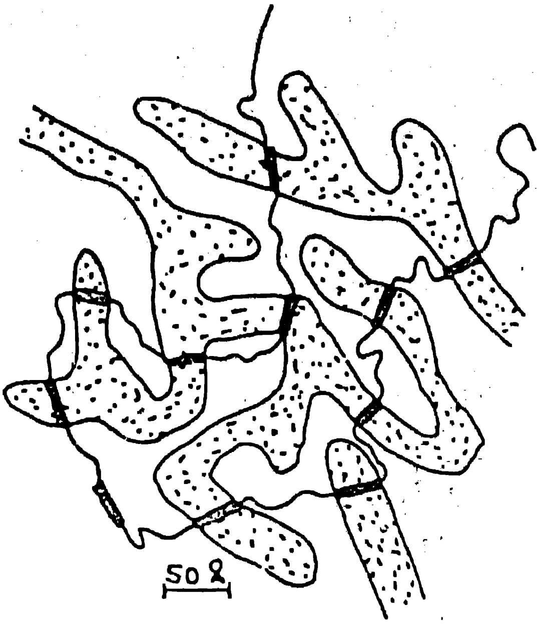


Fig. 2 Schematic representation of domain structure in segmented polyurethanes (hard blocks polyol soft blocks) (Taken from Ester, G.M., Seymour, R.W., Cooper, S.L., Macromolecules, 4, 452, 1971).

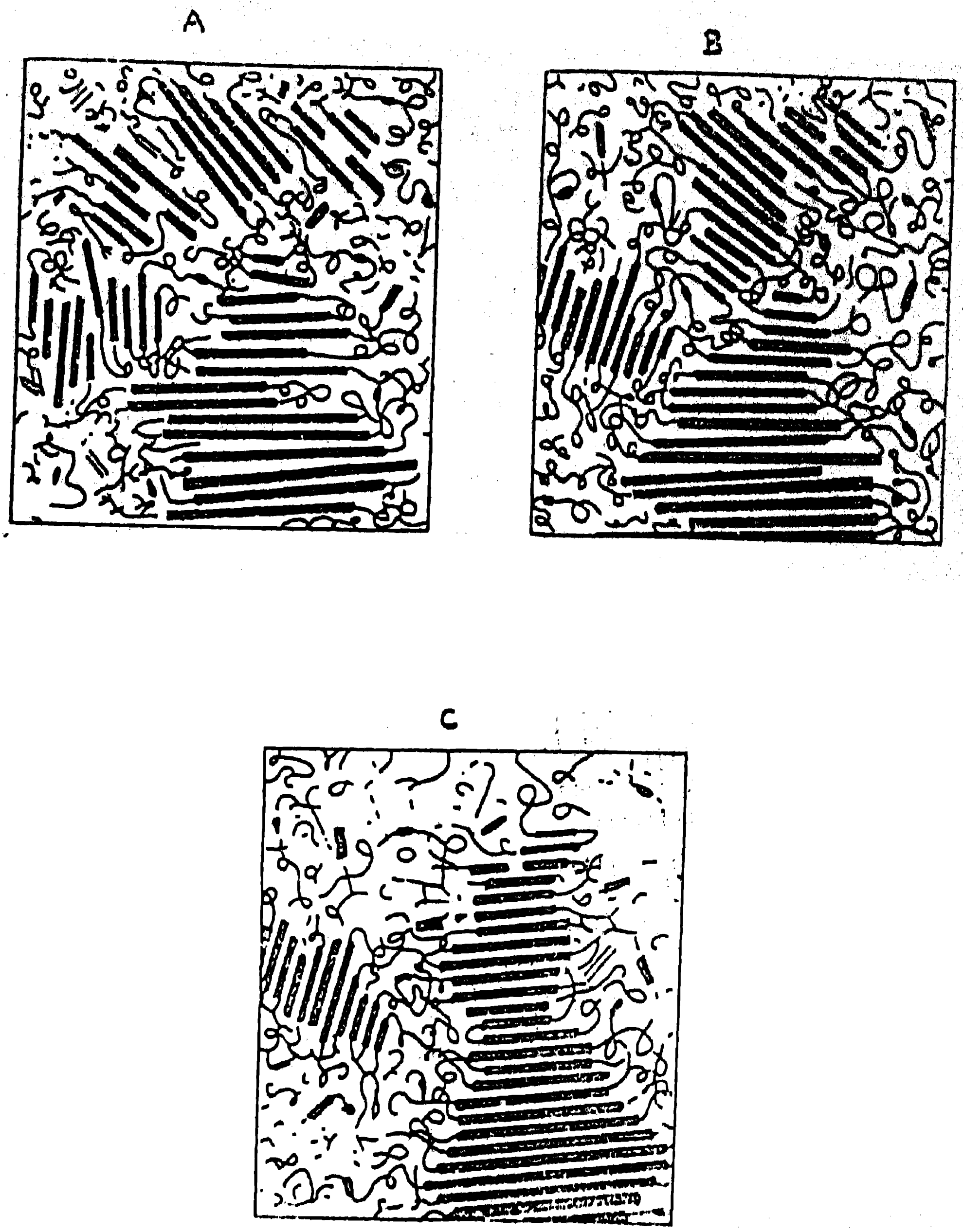


Fig. 3 Schematic representation of degrees of hard-segment domain order A) Lesser ordered , non Crystalline hard segments B) Greater order, non -crystalline hard segment domains C) Microcrystalline hard segment domains (annealed material) (hard segment, soft segment)
(Taken from Hesketh, T.R., Van Bogart , J.W.C., Cooper, S.L., Polym. Engg. Sci. , 20,190,1980).

1.1.2.4 Bulk Morphology Models

The physical properties of polyurethane block copolymer depend much on its morphology various morphological models have been proposed to illustrate the domain structure in undeformed and deformed polyurethane elastomers.

A) Irregularly shaped soft and hard segment domains of any undeformed polyurethane form dispersion. Both phases are contineous and interpenetrating.In most of the instances, the soft and the hard blocks are joined at the domain interphases however, as phase segregation may be incomplete some of the urethane blocks are also disperserd in the rubbery matrix. As both soft and the hard phases are interpenetrating the large deformation of one is impossible without similar deformation of the other, the domain size in the direction of chain axis is approximately 15A°.

B) In elongated polyesterurethane, the hard segment are arranged in a pattern which inhances the formation of maximum number of hydrogen bond between the N-H and O=C group in adjacent segments.

At 200% elongation the stress induced crystallization of the soft segment enhances further orientation of the hard segments in the direction of elongation. This process is accelerated by annealation of polymer. Which also

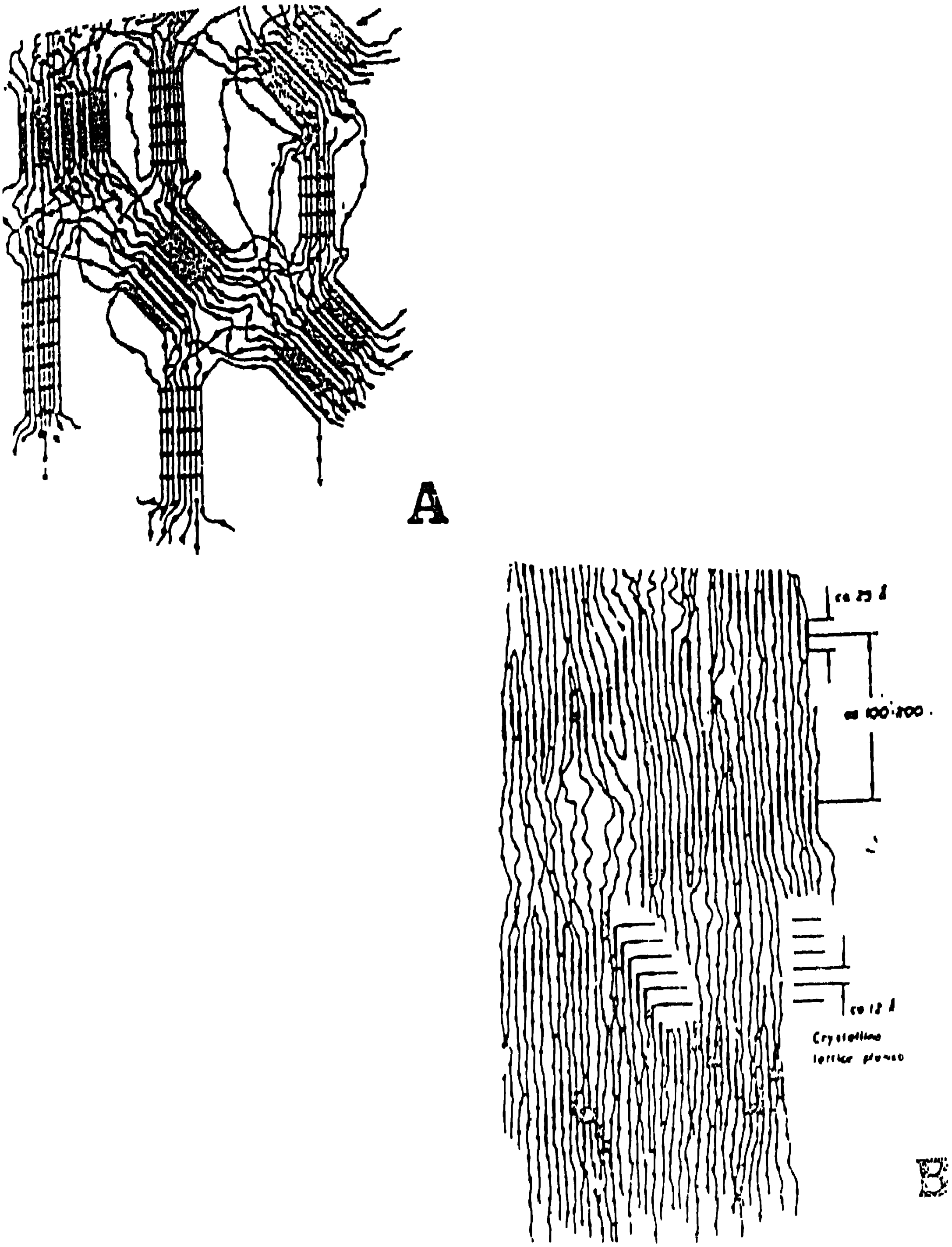


Fig. 4 Morphological model for domain structure in extended polyurethane elastomer. A) Structure of 200% elongation B) Structure at 500% elongation
(Taken from Bonart, R., Morbifzer, L., Hendze, G., and J. Macromol. Sci. Phys., B2, 337, 1969 and Bonart, R. ., Macromol. Sci. Phys., B2, 115,1968).

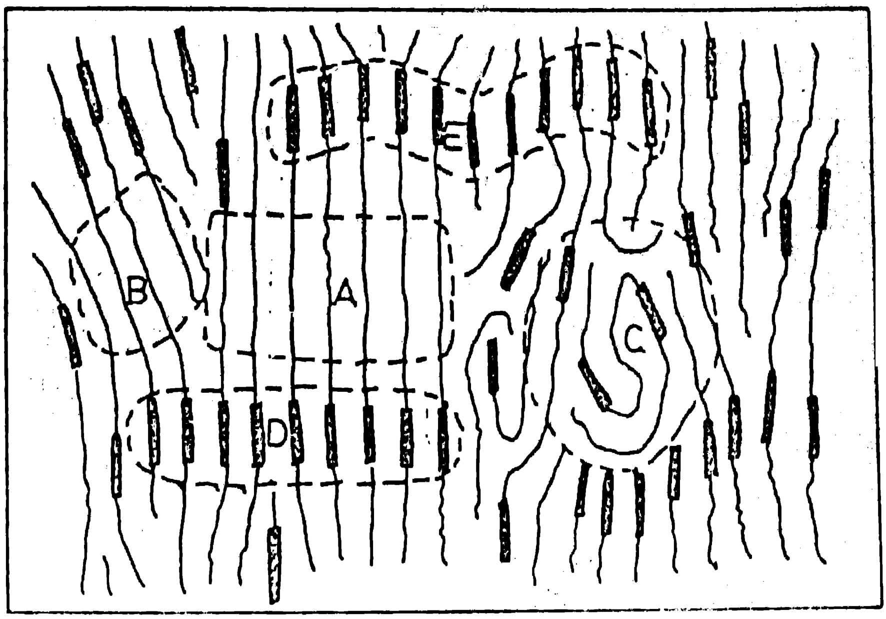


Fig. 5 Morphological Model of segmented polyurethanes after stretching A) Stress-crystallized soft segments) Para crystalline soft segment block ;C) Amorphous "Solution " of hard and soft segments ; D) Crystalline hard segment domain ; E) Para crystalline hard segment domains
(Taken from Wilkes, G.L., Yusek, C.S., and J.Macromol. Sci.- Phys., B7, 157, 1973).

destroys the crystrallinity of the soft segments? Morphology represented by this model exhibits hard segments orientation in the direction of elongation and stress relaxation, disorientation of soft segments.

C) The domains of lamellar shape are formed in polyurethanes stretched to 200-400 %. The average domain size in the direction of the chain axis is in the range of 100-250 A° . Longer soft segments and higher urethane contents lead to higher spacing. The hard segments act as cross links for the system preventing relaxation under stress. The result in the stress induced crystallization of the soft segments, leading to a higher tensile strength.

D) Polyurethanes heat treated at 75 -80 °C at relatively low elongation (100%), undergo spherulitic crystallization, crystalline lamellae consisting of the oriented hard segments float in a matrix of soft segments. The lamellar axis is in the principal orientation axis. At large elongation and higher (500 %, 180 °C) the oriented lamellae disintegrate in to small fragments. The hard segment axis turns out to be principal orientation axis. The amorphous soft segments which compose the matrix, act as tie chains between the lamellae. The paracrystalline structure of polyurethaneurea fiber , heat treated in a highly stretched state , consists of the less ordered fragments of the hard segment lamellae aligned to the fiber axis , while the soft segments appear to be relaxed even in the highly oriented fiber structure .

F) In polyurethane elastomers with polytetramethylene diphenyl methane carbamate hard segments, the planar Zig - Zag - CH 2 - CH 2 - sections connect sucessive

diisocyanate units. The chains are linked together in stacks through - C = O......NH - hydrogen bonds, which involves half of the urethane groups. The remaining urethane groups are similar hydrogen bonded to adjacent stacks, and thus the structure is stablised by hydrogen bonding in both direction perpendiculars to the chain axis.

1.1.2.5 Bulk and Surface Properties of Polyurethane

The surface of material acts as a direct interface between the bulk of material and the external world.The surface therefore is subjected to more attack and alteration by external forces. Though, there is no demarkcation between the surface and the bulk of material, there is a gradual variation in properties with increase in depth from the surface. The variation in any property from surface to bulk is due to difference in chemical composition. These properties have pronounced effect, on the surface properties of polyurethane. So the surface composition of a polyurethaneurea varies with the processing condition and application environment.

It was reported that the polyurethane casted on glass and nickel mould varied in composition both on air and mould facing surface. However, irrespective of mould composition, a general observation in that, the air facing surface is more concentrated with soft segments, and mould surface is more concentrated with hard segments. An increase in depth profile from air facing surface to bulk

of the material increases concentration of hard segments. The distribution of hard and soft segments at the surface and bulk also depends on kinetics of casting. Slow solution casting of polyurethane results in concentration of solvophilic segments at the surface. This phenomenon is however not observed at higher rate of evaporation.

The solubility parameter , polarity of solvent hydrogen bonding ability are the main factors that control the effect of solvent on casting of polymers .A higher structure enhancing solvent increases soft segment concentration at the surface . A structure perturbing solvent increases hard segment at the surface. The solvent with hydrogen bonding ability influence the formation of Meta stable structure at the surface and also in the bulk.

1.1.3 Physio-Chemical Requirement Adhesive for Lamination

An adhesive is a material used for adjoining two surfaces and laminate is a multilayer structure adjoined by a layer of adhesive. Thus, the basic physiochemical requirement of an adhesive for lamination depents upon:

a) the surface properties of lamination substrate

b) the surface and the bulk properties of the thin flim of the adhesive and

c) The compatibility of the adhereing surfaces with the surface layer of the adhesive.

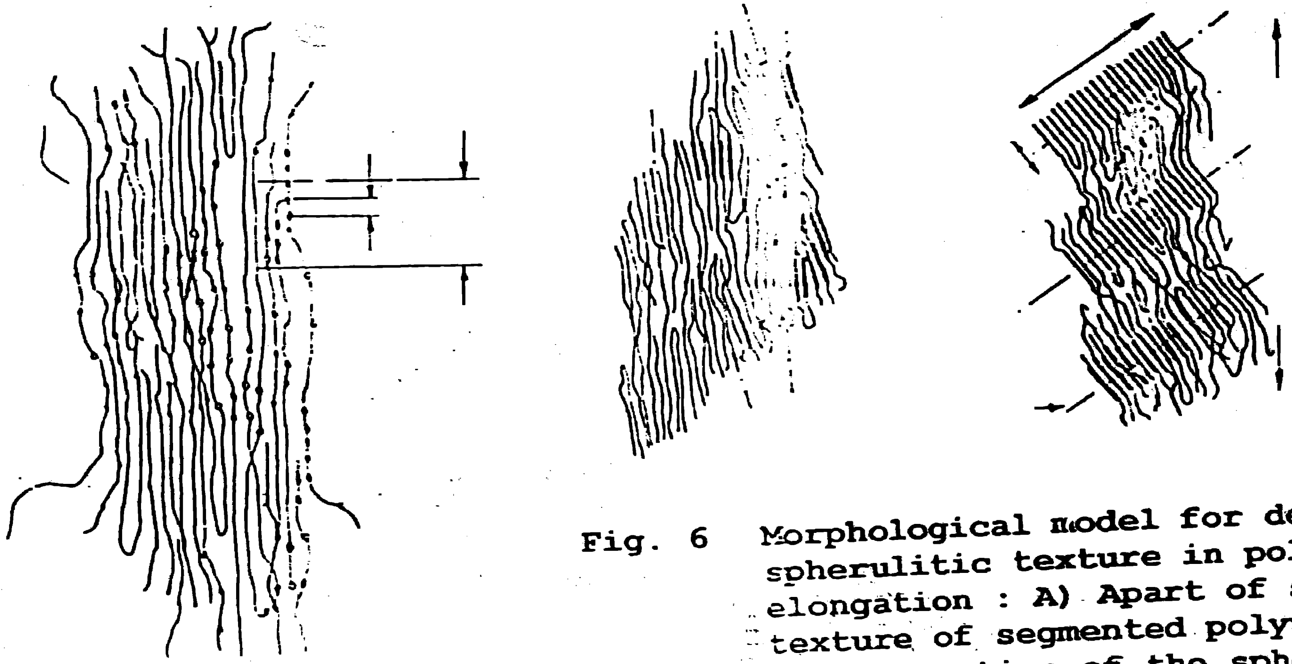


Fig. 6 Morphological model for deformation of spherulitic texture in polyurethanes upon elongation : A) Apart of spherulitic texture of segmented polyurethane urea, B) Deformation of the spherulitic texture upon elongation C) A Model of Structure for highly stretched and heat treated polyurethane urea film (hard segments , soft segments) (Taken from Kimura, I., Ishihara, H., One, H., Yoshihara, N., Nomura, S., Kawai, H., Macromolecules, 4, 457, 1971 and Ishihara, H., Kimura, I., Yoshihara , N., J. Macromol. Sci. Phys., B22, 713, 1983/84).

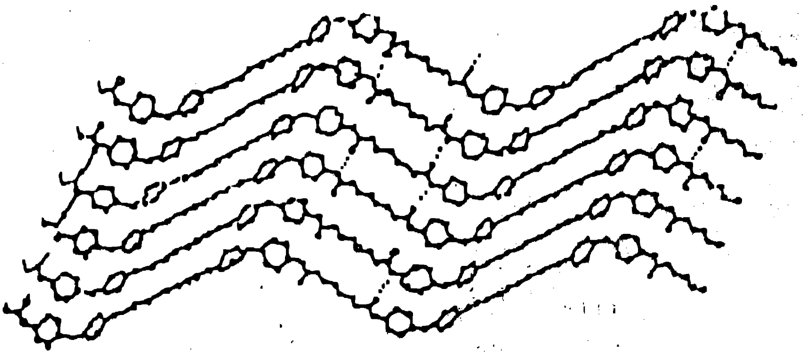


Fig. 7 packing of the Chain in the hard segment domains (Taken from Blackwell, J., Gardner, K.H., Polymer, 20, 13, 1979).

Thus, an adhesive may be suitable for a spceific application may not be suitable for other. (e.g. A laminating adhesive can be used in lamination of concreate metal , plastics etc.but may not be suitable for tissue adhesion)Therefore, in the present study, we will restrict ourselves to polymeric synthetic film lamination. These laminate have many appliction but we will discuss only packaging application.

The material used for packaging application using polyurethane adhesive are Polyethylene terephthlate(PET), Polyethylene(PE),polypropylene(PP),Polyamide(PA),polyvenyl chloride(PVC) ,Ethylene propylenediene monomer(EPDM) and its copolymer . These materials are discussed in details in minor desertation.Therefore, only the adhesive portion is delt here.

Looking at the wide range of laminates and their surfaces , the property of the adhesive must be customerized so that the interaction of the adhesive with a wide range of substrates results in requisite adhesion .Alternatively, the adhesive should have flexibility to adhere to all the above stated substrate to the extend that it is functionally suitable .

Another aspect which is of immense importance is machinability. An adhesive should be versatile enough that it can be suited for any machine other wise a new machine has to be developed for application of the adhesive.

Polyurethane being versatile in character is suitable for most of the lamination substrate.These adhesives are

applied on the substrate in solution form as well as solvent less.

Earlier lamination machine for solvent based and solventless were different but today, same machine can be used for both the lamination.

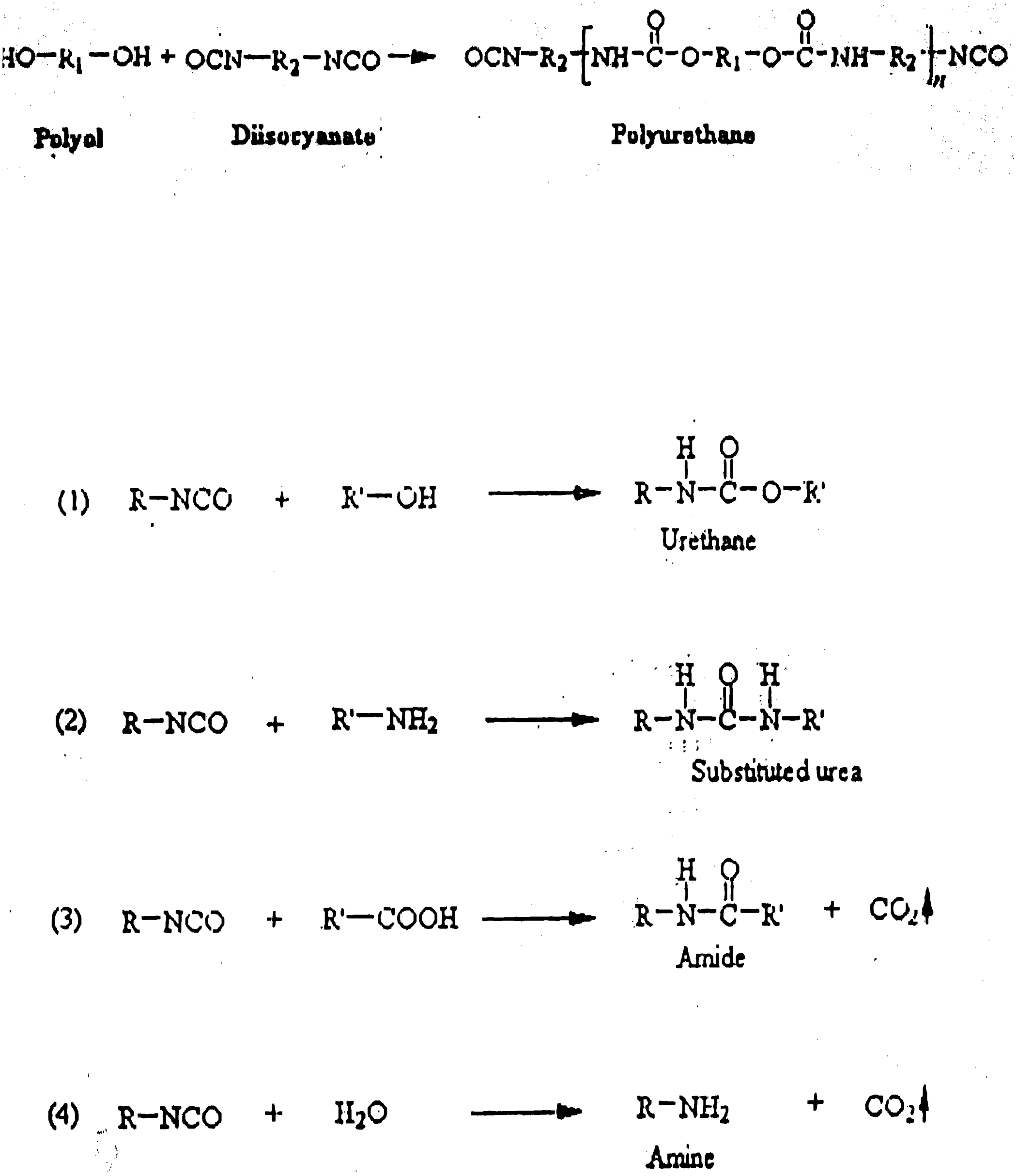
Thus polyurethane adhesive for flexible lamination can be broadly classified as:

1) Solvent based and
2) Solventless

1.1.3.1 Solvent Based Adhesive

Solvent base lamination adhesive are widely used in developing countries. The short coming of this adhesive is the evoporation of the solvent in the atmosphere.This mode of processing makes these materials enviromentally unsuitable (especially for enviromental conscious developed countries). The Indian market of this material is appx. 75,000 MT and the growth rate is approximately 10%.

Chemically, this material are urethane adduct and a polyester base. The urethane adduct is low molecular weight isocyanate ending cross linker available in 75 % solid content solution. While, the polyester component is available at max. 80% solid solution. It is a hydroxyl terminated aliphatic or limited aromatic linear material



$$HO-R_1-OH + OCN-R_2-NCO \longrightarrow OCN-R_2-\left[NH-\overset{\overset{O}{\|}}{C}-O-R_1-O-\overset{\overset{O}{\|}}{C}-NH-R_2\right]_n-NCO$$

Polyol Diisocyanate Polyurethane

$$(1)\quad R-NCO + R'-OH \longrightarrow R-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-R'$$

Urethane

$$(2)\quad R-NCO + R'-NH_2 \longrightarrow R-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R'$$

Substituted urea

$$(3)\quad R-NCO + R'-COOH \longrightarrow R-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-R' + CO_2\uparrow$$

Amide

$$(4)\quad R-NCO + H_2O \longrightarrow R-NH_2 + CO_2\uparrow$$

Amine

Figure A: Primary reactions

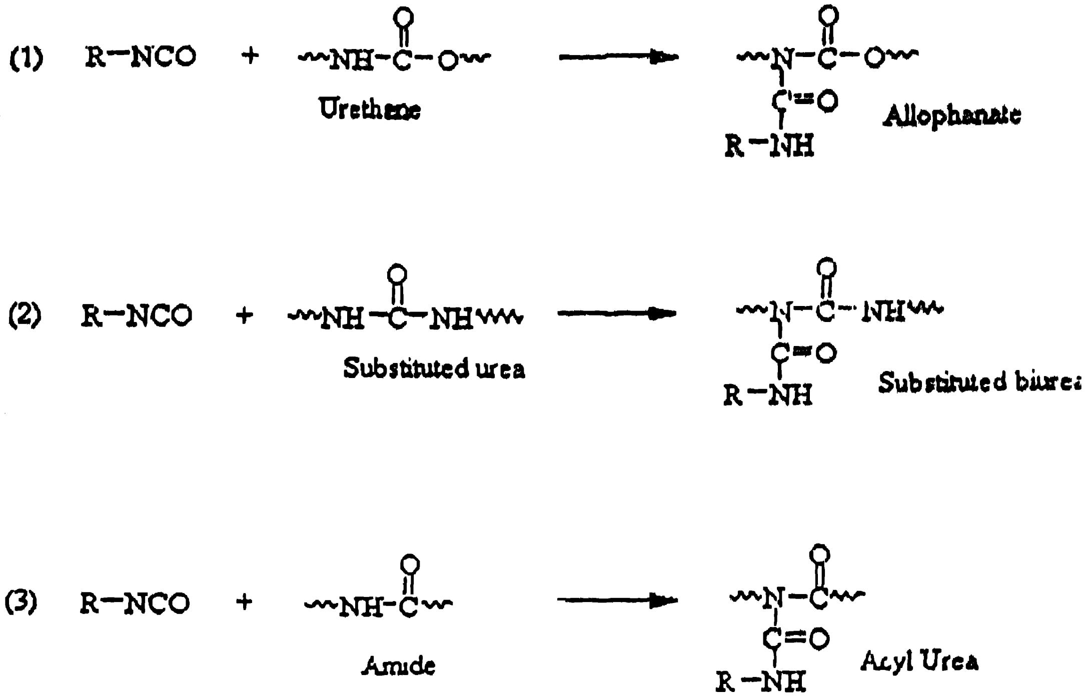
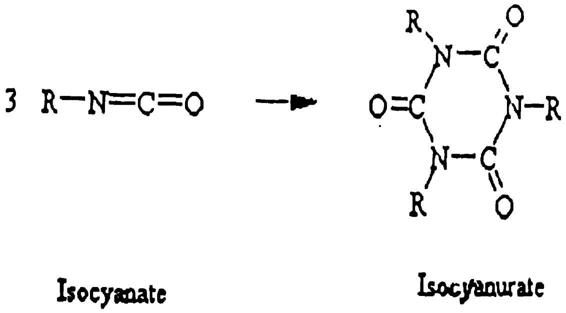
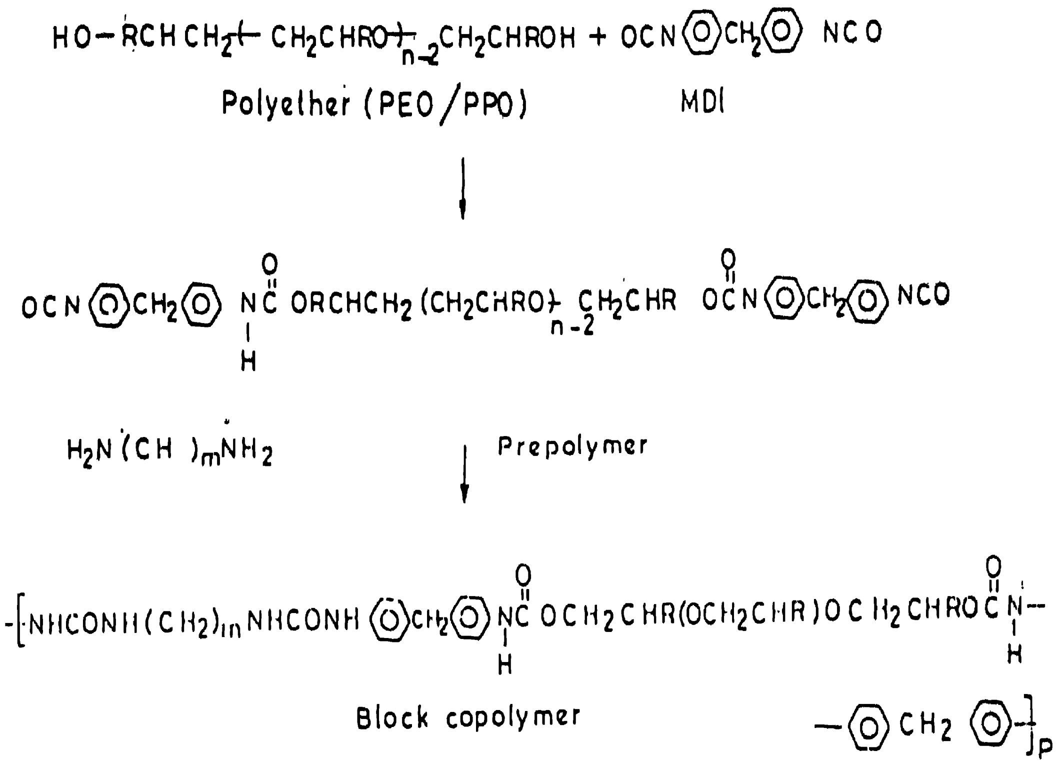


Figure B: Secondary reactions





R = H or CH_3

n = Degree of polymerization of polyether

m = No of methylene group in diamine

P = Degree of polymerization of block copolymer

Schematic representation of reactions involved in the synthesis of block copolymer.

with the molecular weight variation of 15 to 30,000 dalton. This material on mixing with isocyanate component forms a semicrosslinked structure (with low cross linked density). The material is coated on lamination film using a coater (150 lines per square inch roller in the GSM range of 1.0 to 3.5).

A coated material is required to be cured for about 12 hrs. For futher processing, However, total chemical curing takes about 10 days. This material is used in lamination of general products to corrosive and oily products.

However, in food packaging, it is generally avoided. The basic reason is the entrapment of residual solvent between two layers which deteriorate the quality of packed products.

This problem can be avioded using solventless adhesive.

1.1.3.2 Solventless Lamination Adhesive

Solvent less lamination adhesive is available in three basic classes:

i) One component,

ii) Two component and

iii) Water based.

The water based are aqueous polyurethane dispersion or emulsion. Polyurethane water based lamination adhesives are not popular in India because of high investment on laminator, however, these are growing in western countries mainly due to environmental reason and low temperature climatic conditions . These materials are also an alternative to solventless one and two component system. The low temp climates generally result in precipitation of one of the component of solvenless adhesives. While in tropical countries like India these do not pose any such problem. In fact, solventless one component and two component system have paved its way in the national lamination market. Present consumption of solventless adhesive in India, is approximately 1200 MT. It is rapidly increasing at the rate of 18-20%. The reason for its increaseing demand in India is processing speed or productivity and low manufacturing cost at convertors end. Apart from these, the comparative advantage of solventless adhesive over solvent based laminates is given below.

Properties	**Solventless**	**Solventbase**
Cost of Machine	High	Low
Processing Speed	Very high	Comparatively Low
Coating GSM	Low	High
Environmental	Environmental	Hazordus

	Friendly	
Monomer Migration	Lower	Comparatively High
Barrior Properties	Lower	Higher
Mechanical Properties	Lower	Higher
Flexibility	More	Less
Clarity	Good	Lower
Heat Resistance	less	Good
Wettability	Poor	Very Good
Peel Bond Strength	High	Comparatively Low
Curing Duration	Lower	Higher

Inspite of all these advantages, the material did not find its way in Indian market earlier because of two reason, high cost of machine in comparison to solvent base laminator and non availability of technology. Here, we aim to study and subsequently develop solventless lamination adhesive technology.

The adhesive is mainly consumed by corporate lamintor. The main reason behind it is the cost of solventless lamination machine .However, in last half of decade, Indian machine manufacturer have started looking for option of manufacture of the machine. The cost of machine has lower down to 25 lacks from 2 crore. The adhesive that are generally used are in these machine are mainly two component solventless. One component adhesive appears to the convenient but could not attend popularity because of its requirememt of specific humidity condition .The two component adhesive used today, in India, solventless machine uses a fifth generation adhesive . But before we take up fifth generation, following is a brief history of solventless lamination adhesive.

1.1.4 History of Solventless Adhesive

A brief history of solventless lamination adhesive is presented below. These materials are low viscosity and work on the same principal as solvent based adhesive. The two components adhesive is composed of a hardner and a base. One of the components (between the hardner and the base) is isocyanate terminated prepolymer. It reacts with hydroxyl component (other component) upon lamination

leading to urethane bond formation.There are two technologies available in international market and the nomenclature of the hardner and the base is varied accordingly.

Solvent less adhesive technology was introduced in the International market in 1974-1975. It was first developed in 1968; this adhesive was moisture curable single component isocyanate terminated polyether. It was mainly introduced for paper to polyester lamination. The problem with this adhesive was availability of moisture during processing. In varied humid condition, however, some of the isocyanate migrates leading to urea and amine formation. The amine migration is the problem for food packaging application. This led to adhesive to development of adhesive of high molecular weight isocyanate terminated component. But this did not serve the purpose leading to development of reverse solventless lamination adhesive technology (the conventional OH terminated Base played the roll of hardner and the hardner played the roll of base). This reduced the problem to certain extent and finally the fifth generation reverse technology reduced the problem extensively (The migration of isocynate terminated product migration was limited to 0.02ppm).Today, fifth generation two component solventless lamination adhesive is widely used internationally. It has a compliance with FDA 177.1390. It can be used for wide range of products(e.g.it can be used for snacks and candy to hotfill and boilable and sterilizable material , These are oil,alcohol , iodine resistant, these are also used for high temperature packaging) . The only lacuna of

this material is the high viscosity. This lead to slippage problem during lamination. This work is an aim to analyse and modify the adhesive to overcome this lacuna.

1.1.5 Development of Lamination Adhesive

Filling of lacuna is only possible when the past technology and its related problems are clear.Following table shows the history of development of polyurethane adhesive.

Solventfree
Reverse
Two components

Solventless two components
Adhesive system

Solventless one component
Moisture cured

Laminating resin in solution
PET/Polyether with OH/NCO facts

Solution PU/PET mixture
Cured with Polyisocyanate

1950 1960 1970 1980 1990 2000

It can be seen that polyurethane adhesive based lamination started about 50yrs back. The adhesive system was based on polyester urethane elastomer and polyisocyanates .With the increase of demand for the adhesive, the performance requirement became more stringent. Thus polyesterurethane technology only could stand in solvent based flexible lamination market. The majority of user of solventless adhesive demanded high performance, low viscosity adhesive. This led to the development of third generation adhesive .An adhesive that is specifically adapted to the dry laminating field of application. These were based on pure polyester and polyether. Polyester and polyether resin with hydroxyl functions combined with prepolymers having NCO function reacts insitu to form urethane.But the low viscosities of the base and hardner led to the problem of monomer migration .This resulted in the development of medium molecular weight base and hardner. This class of material being higher in molecular weight than the previous class, it is also considered to be high molecular weight. But, it has a molecular weight less than polyesterurethane elastomer therefore it is proper to call it as medium molecular weight.

With this class of adhesive it is possible to achieve adequate initial strength and excellent final properties (such as high laminate bond strength, good adhesive resistance to thermal, chemical and mechanical forces).

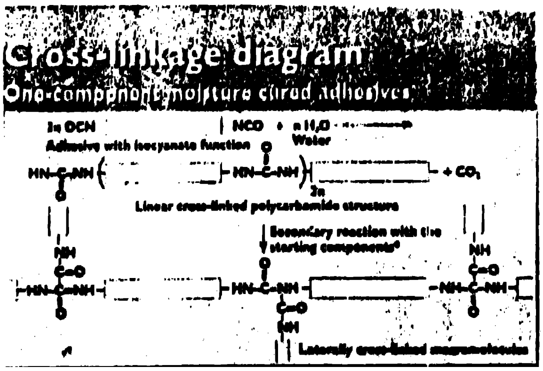
A new era thus began for converters with two component system .But the first development of Herbert's single component still stand in the market.

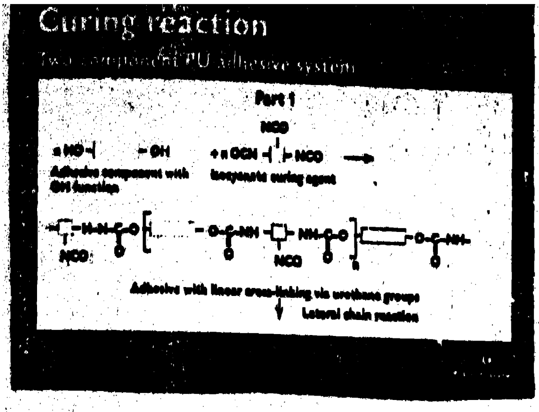
1.1.5.1 Single Component Adhesive

Single component adhesive system is generally polyether urethanes bonded to aromatic isocyanates and are commonly used for lower performance applications. This material need to be heated to 80-90°C to reduce their viscosity for application. These classes of material require moisture to cure. The moisture enters the adhesive from atmospheric humidity. A minimum amount of ambient moisture must be present for complete the reaction .However, this is not of concern in warmer, humid climate. For consistant performance humidification at the lamintion nip is recommended to assure adequate moisture is present to compleate cure. Humidification is accomplished by introducing humidity as a very fine water spray or steam. The humidification system is usually directed at the secondary web. It is not sprayed directly on the adhesive. Water droplet are not sprayed or dropped on to the web.

The adhesive react via a number of secondary stages releasing carbon dioxide. To start with, this reaction is linear via carbamide groups and then via the biuret groups resulting in crosslink polymer matrix.

Chemical Reaction

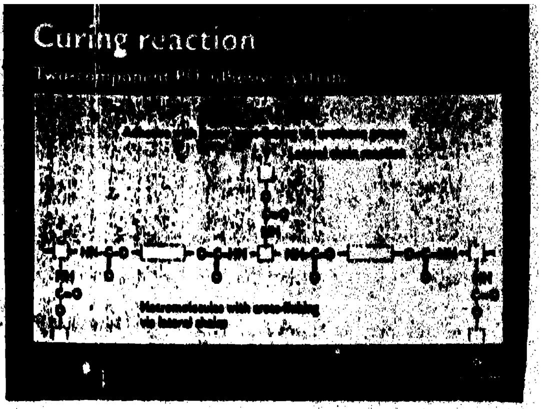

Cross-linkage diagram
One-component moisture cured adhesives
2n OCN
NCO + n H₂O
Adhesive with isocyanate function
Water
HN-C-NH
HN-C-NH
2n
+ CO₂
Linear cross-linked polycarbamide structure
Secondary reaction with the starting components
NH
C=O
HN-C-NH
HN-C-NH
C=O
NH
NH-C-NH
Laterally cross-linked macromolecules



Curing reaction

Two component PU adhesive system

Part 1
NCO
HO
OH
OCN
NCO
Adhesive component with OH function
Isocyanate curing agent
NCO
NCO
n
Adhesive with linear cross-linking via urethane groups
Lateral chain reaction



Curing reaction

Two component PU adhesive system

The So called water reaction is slow enough to consumed the adhesive in pan .Life is sufficient long to allow adhesive application through the scoll shits to the bath without , even at extencively high conversion temperature.

In practice, limitation results from relatively high moisture requirement in the region of 10 mg per gramme of adhesive. The thermal load ~~to~~ which web is substrated and risk of blistering due to Co2 when laminating gas tight substrates.

For this reason, one component adhesive is mainly used for paper laminations which have a sufficiently high moisture content and adequate gas permeability. Film lamination can also be bonded if suitable air conditioning is provided or in presence of sufficient moisture with ambient pressure of sufficient moisture In the ambient air is assumed by mean of water vapour introduced through the laminating slits.

1.1.5.2 Objective:

The aim of this project is to synthesis solventless flexible lamination adhesive with reverse technology having negligible slippery problem during lamination.

1.1.6 Plan of Work

The work is planned in following chapters

1) Selection of raw materials Charecterization methods and Processes
2) Result and discussion
3) Conclusion and Future Scope

CHAPTER - 2

SYNTHESIS AND CHARACTERIZATION

2.1 Selection of Raw Materials

The aim of this project is to synthesize solventless polyurethane adhesive for flexible lamination appliaction. It has been explained that the raw material used for this application are polyethers derived from cyclic ethers and polyester derived from diols and diacids. Three type of polyethers based on cyclic ether were selected for this project, namely

i) Ethoxy ether
ii) Propoxy ether and
iii) Tetramethoxy ether.

These were procured from SIGMA Chemicals USA. The diols used in the synthesis of polyester are 1,2 Ethylene glycol, 1,2 Propylene glycol ,1,4 butane diol and 1,6 hexane diol . Two diacids were used, namely

I) Adepic acid and
II) Phthalic acid

While Toluene diisocyanate and 4, 4′ - Diphenylmethane diisocyanate were obtained from TMI Japan.

2.1.1 Catalyst

Catalyst play dominant roll in the synthesis of these materials, many catalysts are known to be used in solventless lamination adhesive.However, Tin and Amine catalyst are dominantly used for these synthesis.It was observed that tin octoate and triethylene amine are the most suitable catalyst for this work. These are obtained from Aldrich chemicals, Germany.

2.2 Method of Synthesis of Solventless Adhesive

Solventless two component adhesive were synthesized in parts. Intially, polyether was prepared followed by polyester, polyesterether and polyurethane. These are explained as follows

2.2.1 Methods of Synthesis of Polyethers

Polytetramethoxy glycol was synthesized at 4°C using trifloro sulphuric acid 0.01% as catalyst in a compleately dry atmospheare. The atmosphere and tetrahydrofuran are first dried in calcium hydried for 48 hrs at room temperature. These are directly transfer to the reaction medium having an anchor stirrer attached to it.Catalyst is slowely pored in to the reaction medium at 4 °C through a pressure syringe .The reaction takes about 4 hours to complete . The counter ions are removed from the chains by

hydrolysis. The total process takes about 12 hours to complete. The final material is purified by using vaccum at 760 mm of Hg. The total process of purification takes about 6 hours.

2.2.2 Method of Synthesis of polyester

The raw materials (diacid and diols) were charged into a one litre four necked reaction kettle equipped with a taflon blade glass stirror. The flask was kept on heating mantle (thermally insulated) and was attached to a condenser through a T joint. The content was mixed at 100°C.The temperature was then gradually increased to 220°C over a period of 12-14 hrs. Finally vacuum was applied for a period of 6-8 hrs to reach to requisite molecuar weight.

2.2.3 Method of Synthesis of Polyether-ester

The material were synthesised by similar method excepting the fact that polyethers were used along with diols and other monomers of polyester.

2.2.4 Method of Synthesis of Urethane Ester and Ether Ester

The calculated quantity isocyanate in dry toluene was taken in four neeked flax fitted with nitrogen inlet, stirror and addition vessel. The ester or polyetherester

was dropped through addition vessel in the reaction vessel with continuous stirring in a period of one hour. The reaction vessel is then slowly heated to 75°C and maintained at this temperature for 6 hrs. The final product is then poured out from the reaction vessel at room temperature.

2.2.5. Chemical Method Characterization

The synthesized materials were characterized for chemical analysis by Infrared spectroscopy·

2.2.5.1 Method of Characterization by Infrared Spcetroscopy

The material was casted on KBr pallet. The peak at around 3400 Cm-1 is due to NH streching. The peak at 2900-3000 Cm-1 is due to CH streching. The peak at around 1600 Cm-1 due to aromatic stretching. The peak at 1700 Cm-1 is due to CO stretching. The absences of peak at 1100 Cm-1 suggest that this is no etheral compound and ester base compound. The peak at 1700 Cm-1 and 3400 Cm-1 suggest that it has a buirete hence it is an isocyanate containing aromatic biurirets.

2.2.6 Method of Physical Characterization

2.2.6.1 Molecular determination

The molecular weight was determined by gel permeation chromatography. The chromatograph was run by using a universal column having RI detector. Tetrahydrofuran was used as mobile phase. It was observed that the material is in the molecular weight range of (weight average) 2000-4000 and number of average 1000-2000 with molecular weight distribution of approximately two . The absence of any peak below 1000 or above 4000 suggest that the material is free from unreacted monomer or oligomers and it has narrow distribution in single range (molecular weight) of material and it is not a blend of polyester and polyether.

2.2.6.2. Determination of Viscosity

The viscosity of material is determined by Brookfield viscometer using spendle number 3 to 5 at 30 °C.

2.2.6.3. Casting of Laminates

The hydroxyl and isocyanates component were mixed in different ratio and casted over polyester, BOPP & PVC by a bar coater and covered with polyethylene, CPP, Met Pet, Met BOPP & PVC. Then material was passed through a document laminates machine and kept under pressure for 24 hrs. The initial bond strength is almost zero with no tack on the casted surface. The materials generate tack after 2 hrs. or so and the tack vanishes within 24 hrs

times leaving the structure compleately bonded to each other. The bond strength was determined using an Inston tensile testing machine.

2.2.7. Bond Strength

The laminate was cut in 1.5 cm width. One edge was gripped by stanatioary grip and other by movable grip of the peel bond testing machine. The material is evaluated for bond strength by T peel strength tester . The load cell of machine is adjusted so that it has maximum loadibility of 1 Kg . Various synthesized materials were mixed in different ratio . These laminates had different peel bond strength range from 50 to 700 gms/15mm. The peel bond strength varies with compositions. It was generally observed during this study that the bond strength increases with increase in hydroxyl compponent in the adhesive .With the increase in isocyanate component, the material stiffness increases. This may be due to increasing aromatic portion of adhesive .The grams of the transfer of the adhesive was determined by the method given below .It was observed that if the grams increases, the bond strength is increases up to certain extent and then become constant . This may be due to the fact that with increase in gsm, increases the cohesive forces in the adhesive. Thus the force in the material is distributed more to the adhesive material than the substrate and finally it becomes constant. The later may be attributed to the fact that the distribution of this force remains unaltered after coating an extant of adhesive quantity.

2.2.8. Evaluation of Adhesive Coating Gramages

The both component of adhesive mixes together through a mixing pump in respective porportion and put in between application and metering roller , the temperature as well as tension parameter is then set . The machine is than started and the speed is increased to actual running speed. A adhesive coated sample is collected and weighed. The adhesive is washed out with help of solvent. The difference between weight of substrate and composite calculated.

CHAPTER -3

RESULT AND DISCUSSION

The synthesized materials were subjected to instrumental analysis using following techniques.

3.1 Spectroscopic Analysis

The hydroxyl component was spectroscopically analysed using FTIR. The result is presented in figure 8. The peak at 3400 Cm-1 correspond to OH group .The were 3000 Cm-1 is due to CH2 and CH3 streching. The absorption at 1750 Cm-1 and 1000 Cm-1, may be due to ketonic and ether linkage and peak at 1600 Cm-1 is due to aromatic carbon. This suggeste that the material is a polyester polyether having hydroxyl end. The presence of hydroxyl as well as ketonic group could be due to acid or ester linage or ether and ketonic functional groups also .This was verified by acid number and hydroxyl number

3.1.1 Hydroxyl Number

Table 1. presents hydroxyl number of various synthesised materials .It was found that the hydroxyl number are in the order of 100-120 which the materials

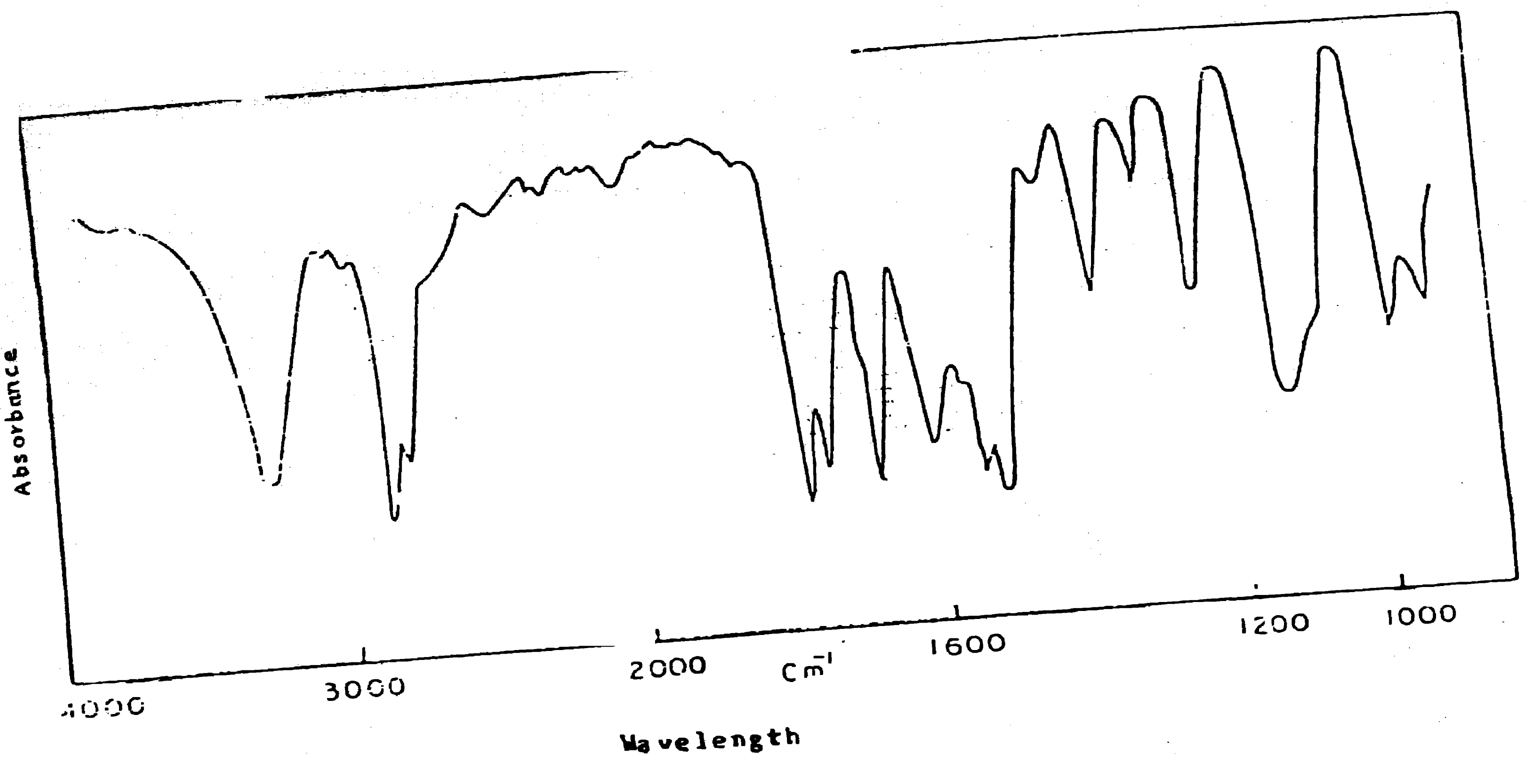


Fig. 8 Representative infra red spectrum of Synthesized Polyurethane.

TABLE NO. 1.0

HYDROXYL NUMBER ,ACID NO AND APPARENT MOLECULAR WEIGHT

S. No.	Hydroxyl No.	Acid No.	Mol. Weight
1	100	0.2	1120
2	102	0.5	1098
3	105	0.7	1066
4	109	0.3	1027
5	115	0.4	973
6	118	0.3	949
7	120	0.6	933

have very low acid number . This is below 1. Thus the apparent molecular weights of the components are presented in the table 1.

Since the molecular weight was determined considering the fuctionality as 2 so actual molecular weight was dertemined using gel permiation chromatograph taking polystyrene as standard, the molecular weight of the material are presented in the table 2. It may be seen that the relative molecular weight are in the range of 2000 to 5000 amu with a distribution of two. Thus the number average molecular weight is with the range of 1000 to 2500. This is in accordance with requirement of sloventless lamination composition. A low molecular weight polyester result in a high fluidity, therefore, mixing of the components is convenient. The fludity of the synthesised material was varified by viscometric method.

3.1.1.1 Brooke Field Viscosity

The viscosity of the material was calculated at room temperature. Table 3. presents the viscosity of the material. It may be seem that the viscosity varies from 1400 cps to 3000 cps. This is in comparison to standard product obtaining from market. Thus the material flow is sufficient for the application of the product by mixing with isocyanate component.

TABLE NO. 2.0

MOLECULAR WEIGHT OF VARIOUS SYNTHESISED POLYURETHANES

S.NO.	NUMBER AVERAGE (Dalton)	WEIGHT AVERAGE(Dalton)	POLYDISPERSITY INDEX
1	1200	2450	2
2	1350	2600	1.7
3	1500	2560	1.7
4	1798	2525	1.4
5	1840	2560	1.4
6	1920	2580	1.3
7	2020	2800	1.4
8	2500	3200	1.3

3.1.2 Spectroscopic Analysis of Hardner

The spectroscopic analysis of the isocyanate component is presented in figure 3. The peak at above 3400 Cm-1 may be due to N-H streching. The peak at around 3000 Cm-1 is due to CH, CH2, and CH3 streching. The absorption around 2100 Cm-1 may be due to NCO group. This is followed by 1700 Cm-1, 1600 Cm-1 & 1000 Cm-1 . These peaks may be due to ketonic oxygen, aromatic group and etherel oxygen . Thus the probable structure of material may contain following group.

1) Carbamate
2) Isocyanate
3) Ketonic
4) Ester
5) Ether
6) Aromatic.

The above study shows that the material is isocyanate terminated polyester or polyether or combination of it.

3.1.2.1 Gel Permeation Chromatography of Hardner

Table 2. Presents molecular weight of various synthesised polyurethane. It may be seem that it varies from 2000 to 3200 with a number average molecular weight of 1000 to 2500. These further suggest that the distribution is approximately 2. It was also found that as

TABLE NO. 3.0

VARIATION OF VISCOSITY WITH MOLECULAR WEIGTH (END GROUP ANALYSIS)

S. No.	VISCOSITY (CPS)		MOLECULAR WEIGHT (Dalton)	
	OH	NCO	OH	NCO
1	3000	1700	3400	2500
2	2500	1600	3000	2300
3	2000	1550	1700	2000
4	1780	1525	1700	1920
5	1700	1500	1673	1900
6	1690	1456	1665	1879
7	1650	1447	1640	1850

the molecular weight increases, the viscosity of the polymer increases. This was varified by viscometry study.

3.1.3 Viscometry Study of the Two Components

The viscosity of various synthesised material is presented in the table 3. It may be seemed that with increase in viscosity, the molecular weight increases. This leds us to conclusion that the material may be mixed to understand the mixing beharivour before making laminate.

3.1.4 Viscometry Study of Mixture of NCO & OH Components

The isocyanate component was mixed with hydroxyl component at various ratio and viscosity of the material was studied at various interval .The table present the mix viscosity of various materials. It may be seen from tables that with the increase in hydroxyl component, the viscocity of the mixture increases.This suggest that hydroxyl component is acting as hardener in this reaction. It is generally assumed that isocyanate terminated component acts as hardener. This reverse behaviour is observed in standard material also.

It may also be seen from the table 4. that the reaction kinetics increase is negligeble in 30 min, in

TABLE NO. 4.0

VARIATION OF VISCOSITY OF VARIATION OF MIXTURES OF NCO AND OH COMPONENT

S.NO.	TIME IN MIN.	VISCOSITY IN POISE AT 30 C
1	10	30
2	20	32
3	30	38
4	40	40
5	50	50
6	60	60
7	70	70

TABLE NO. 5.0

VARIATION OF VISCOSITY OF MIXTURE OF NCO-OH COMPONENTS (cps)

S.NO.	TIME	VISCOSITY AT40C	VISCOSITY AT50C
1	10	1250	600
2	15	1500	900
3	20	1800	1200
4	25	2100	1500
5	30	2550	1950
6	35	3000	2150
7	40	3300	2700

case of mixing ratio of 100 : 50 Isocyanate : hydroxyl components.This is accordance with the standards material.

With increase in temperature, the viscocity of the mix increases as shown in table 4. This is due to increase in rate of reaction of OH to NCO with temperature. As the temperature increases, the required activation energy is attained by more number of molecules. Thus, the rate of reaction is increases. The mixed viscosity of the polymer is closely related to green bond strength and cure time.

3.1.5 Bond Strength

Table 6. present a comperative study of bond strength of synthesised material with some standard materials. It may be seem that the green bond strength of the laminate are very low in comparison to the green bond strengh of the solvent based materials , The green bond strength is directly related to individual material Characteristic of base and hardener and its wettability . The solvent base hydroxyl component being higher in molecular weight with reference to solventless material has more adhesive charecteristic but has low wettability. Table 7. Present the wettability of the various substrates which are comperative with solventless adhesive. This is a important characteristic, a wide variation in surface tension of laminate substrates and adhesive leaves the film patchy. This results in wide variation in final bond strength of the material.

The final bond strength or the bond strength after 24hrs is an important parameter for industry .academically

TABLE NO. 6.0

MAXIMUM BOND STRENGTH OF DIFFERENT LAMINATES

		BOND STRENGTH (gm/15mm)	
S.NO.	SUBSTRATES	1ST DAY	7TH DAYS
1	Pet / Polyethylene	220-250	250-280
2	Pet / Foil	150-200	180-250
3	CPP / Foil	120-160	150-190
4	Met Pet / Polyethylene	150-180	180-220
5	PVC/PVC	350-400	500-600
6	PVC/ Polyethylene	250-300	350-450

TABLE NO. 7.0

WETTABILITY OF DIFFERENT SUBSTRATES

S.NO.	PLASTIC SUBSTRATES	WETTABILITY(DYNES /CM)
1	Polyethylene	38-42
2	Polyester	40-42
3	Corona Treated PET	46-48
4	Chemically Treated PET	50-52
5	Chem.Coated Pet (PVDC)	48-52
6	Chem.Coated Pet (Acrylic)	48-52
7	Biaxiallypolypropylene	38-42
8	Cast Polypropylene	38-42
9	Metallized Polyester	40-42
10	Met Pet (Corona Treated)	46-48
11	Met Pet (Chemically Treated)	50-52
12	Nylon	46-48
13	PVC	36-38
14	PVC(Corona Treated)	40-42

speaking, this is the time in which major reaction between the two components takes place. However, this reaction contineous till 30 days.

The objective of the work is industrial application oriented. Therefore our study after 24 hrs of laminates is equally important.

The adhesive was laminated on various structures namely.

Polyester / Polyethylene
Printed Polyester / Polyethylene
Printed Polyester / Al- Foil
Metallized Polyester / Polyethylene
Printed Bi-axially oriented polypropylene/ Polyethylene

As evident from above, the adhesive was applied with variation in following

1. Ink Variation
2. Ink GSM Variation
3. Substrate Variation
4. Substrate thickness variation
5. Adhesive mix ratio variation
6. Surface energy of substrate variation

3.1.6 Ink Variation

There are three types of inks used in lamination industry, namely

1. Amide
2. Vinyl
3. Urethane

The compatibility of the adhesive with Ink is one of the important factors that control the use of adhesive in flaxible lamination.Polyurethane inks are most compatable followed by vinyl and amide inks. This may be due to similarity in composition of the ink and the adhesive. The result of compatibility is reflected on the bond strength and the sharpness / clearity of the printed zone. Incompatibility is often reflected on the quality of laminate obtained after adhesive application. One of the most common phenomenons is appearence of dots or air pocket or speckling. It is common with white and violet inks . This may be due to following reasons

1. Chemical composition of the pigment e.g. While ink contains Titanium dioxide. Titanium dioxide shows a wettability problem especially when the dispersion of it is not proper.

2. An improper dispersion also reduces the bond strength and

3. Particle size of the pigment.

The problem of speakling and peel bond strength is more related to compatibility of adhesive & ink.

Vinyl ink is most common in Indian market. These are mainly used for printing Polyester, Polypropylene and Polyvinyl chloride surfaces etc.

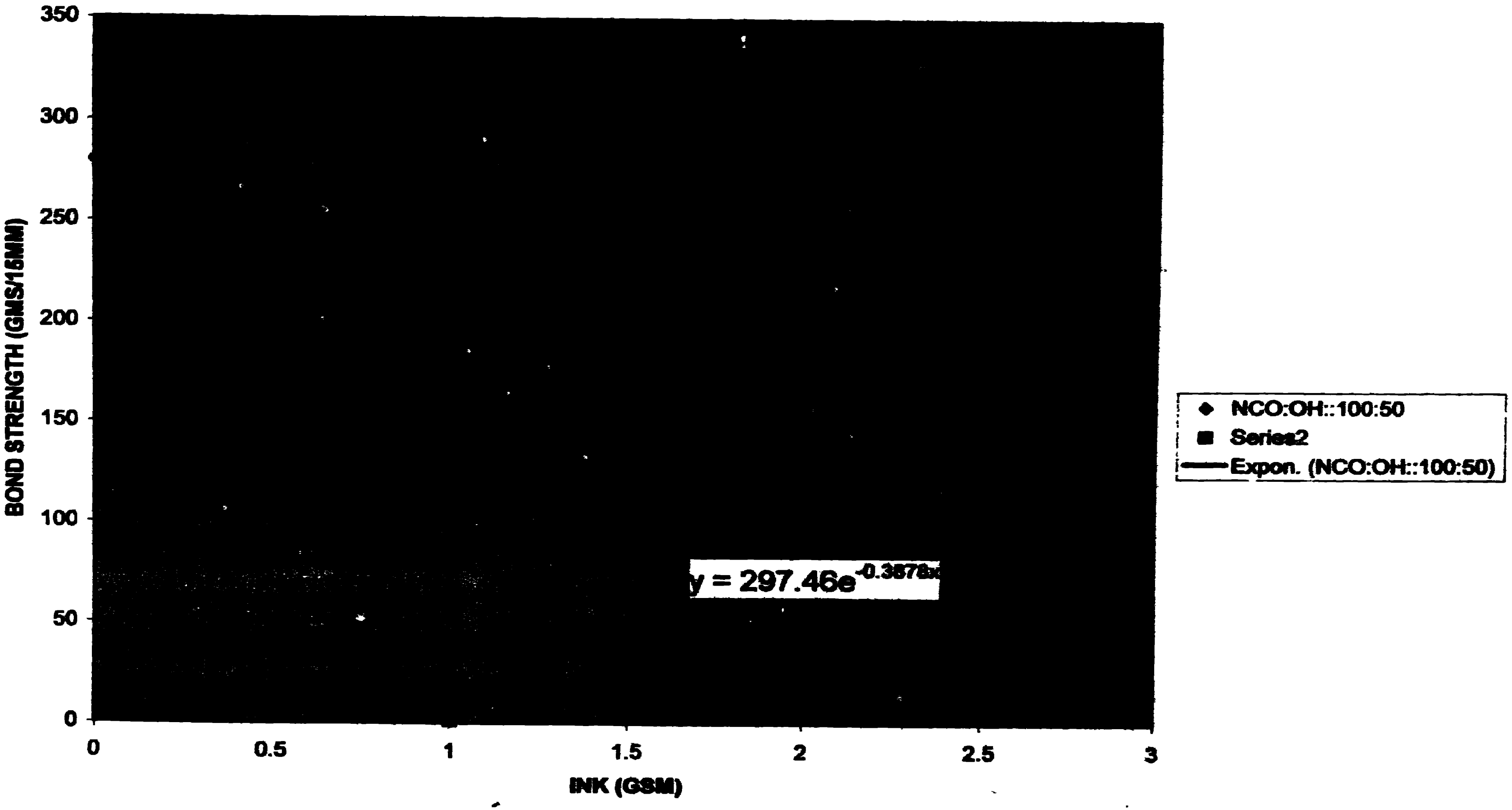
The other surfaces that are printed are Aluminium foil & Polyolefin surfaces. The aluminium sufaces are printed with nitrocellulose while polyolefin is printed with Amide ink especially, when the surface is not treated with adhesive.

Thus, composition of ink and nature of substrate to be printed and the post operation, has close correlation. Apart from nature of ink, the thickness of the ink layer plays a major role in determining the bond strength.

Figure 9. Shows the correlation of ink gsm to adhesive gsm. It may be seen that the increase in GSM of the ink decreases the bond strength.
The decrease may be due to increase in brittleness of the ink layer.

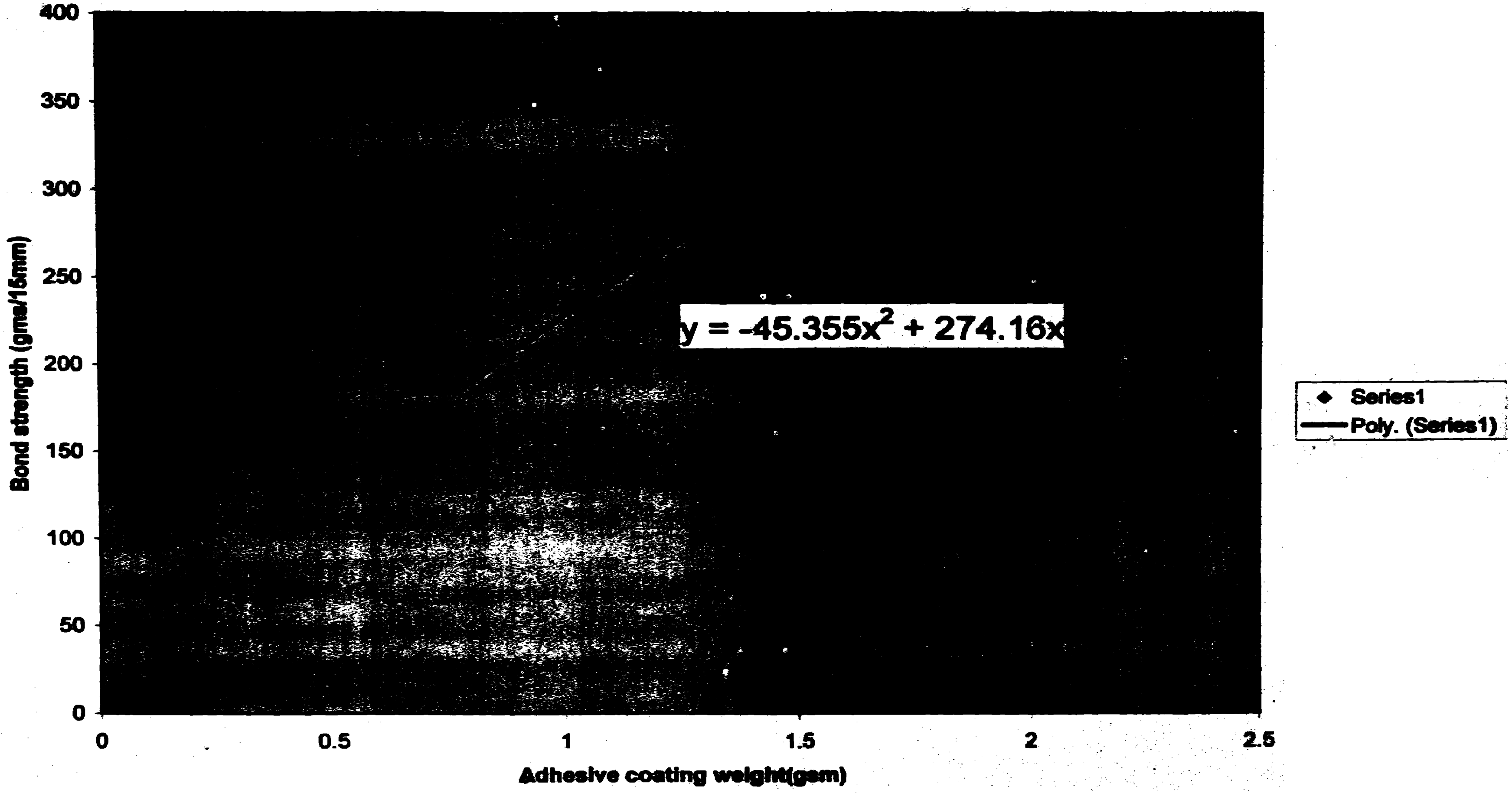
Similarly, an increase in adhesive thickness at constant ink thickness increases the bond strength (figure 10). The increase in the bond strength may be due to wetting of available site for bond . Another phenomenon that may be observed is the transfer of the print layer to the adhesive layer from the vergin polymer layer. This may be due to competitive transfer of site of adhesion from polymer layer - the ink to the ink - adhesive layer. The later takes place, when the force/energy for adhesive - ink is more than vergin film - the print .Thus there is transfer of site of adsorption from the later interlayer to the former.

Different ink also affects the bond strength. This is due to the chemical composition of ink. Many ink contains certain major chemical that decreases the bond strength



VARIATION OF INK GSM WITH BOND STRENGTH IN GMS/15MM

Fig. 9



Bond strength with coating weight

Fig. 10

(e.g. TiO2 in white ink. Similarily, violet ink also decreases the bond strenght).

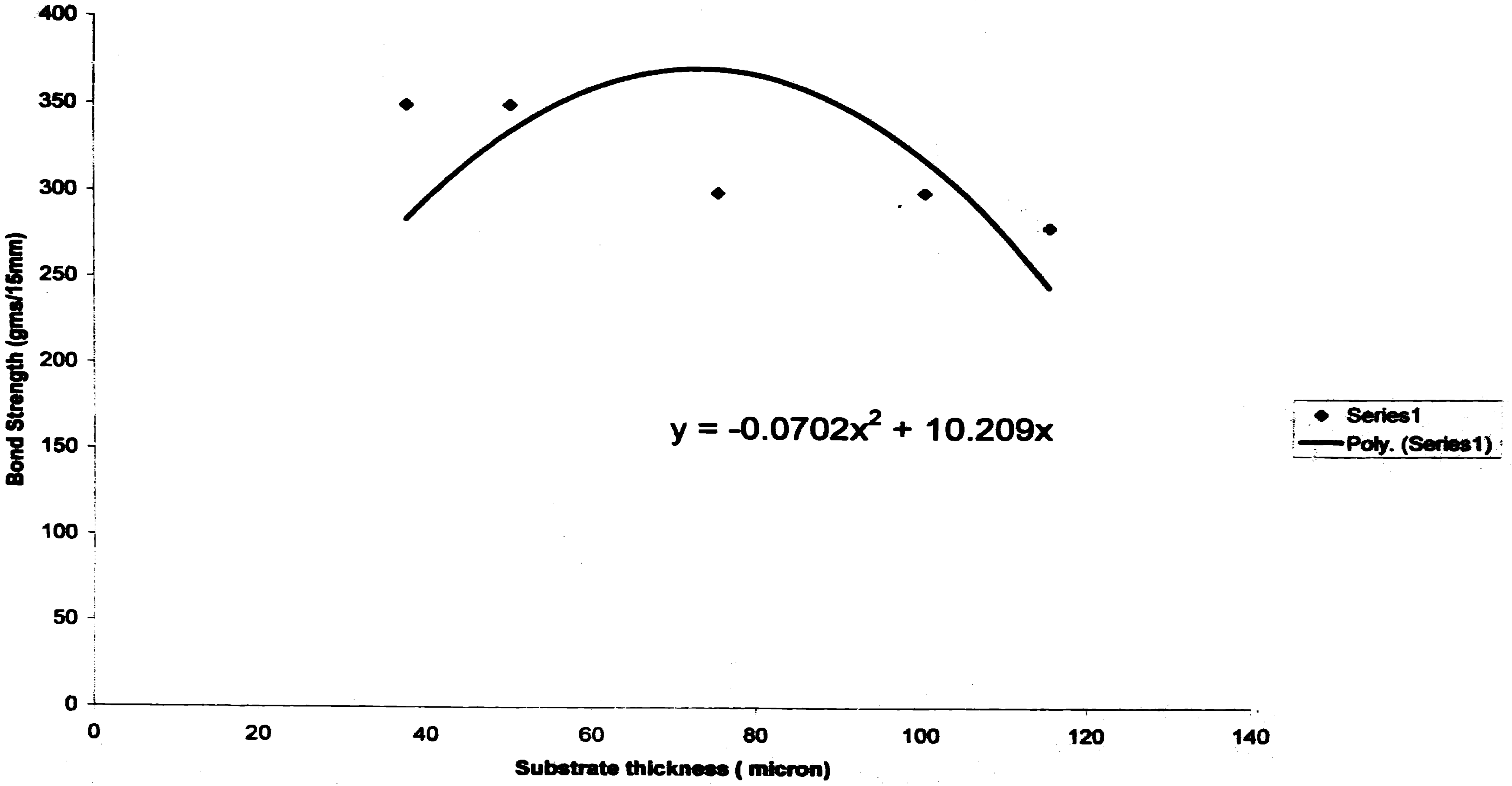
3.1.7 Variation of Bond Strength with Surface Tension of Film

The surface tension of film is varied by corona treatement & chemical treatement. An increase in the surface tension from 38 dynes to 52 dynes/cm, the bond strength of laminate increases. Thus, this may due to increase in active site at the surface.

The surface energy also depend on type of substrate.The bond strength is maximum for nylon based substrate followed polyester and olefinic substrate. This may be due to it bonding ability of amide and ester (H-bond & vander Waal force) .The adhesive bonds the olefinic surface by vander Waal forces only.

3.1.8 Substrate Thickness

Figure 11. shows the variation in the bond strength strength with thickness of polyethylene (poly) on polyester lamination. As the thickness of polyethylene increases the bond strength decreases. This may be due to wettability of polyethylene. As the thickness of polyethylene increases the force transfer during nipping decreases. Thus, the surface of polyethylene that comes in contact with coated polyester surface decreases .Hence,



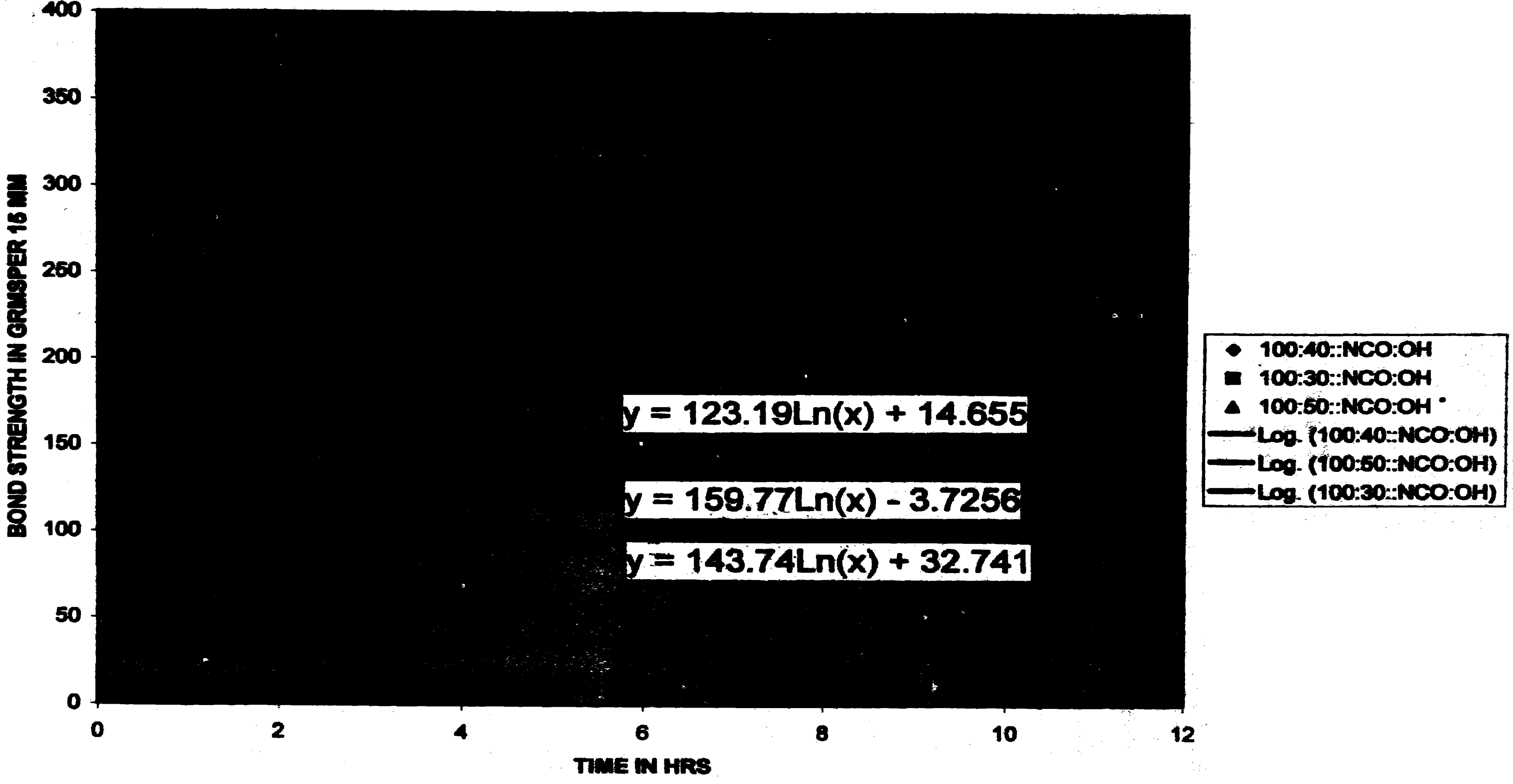
Bond strength with Substrate thickness variation

Fig. 11

the bond strength decreases. This may also be due to increases in stiffness of the polyethylene film. An increase in the stiffness of polyethylene film also reduce the probability of force transfer from roller incontact with polyester film to the roller in contact with polyethylene .This results a decrease in contact of film surfaces (polyester and polyethylene). As a consequences of it , the wetting of the film decreases and finally the bond strength . Another reason may be due to the fact that as the thickness of polyethylene increases , The difference in thickness of film increases the compressibility of the film increases and the force at adhesive surface decreases subsequently the contact force and resulting force of reaction on polyethylene surface decreases.

3.1.10 Effect of Mixed Composition on Bond Strength

Figures 12. shows the variation in bond strength with variation of hydroxyl and isocyanate component of the adhesive. It may be seen that the kinetic of increase of bond strength after lamination and final bond strength increases with increase in hydroxyl component. An increase in isocyanate component decreases the bond strength. This may be due to plasticization of the adhesive layer. An increase in isocyanate quantity results it to exist as such on the laminate without reacting with any other component .This results in increase in inter film layer fluidity. Thus, the bond strength decreases.On the other hand, the bond intially decreases with increase in OH component but subsequently increases. This may be due to kinetics of reaction. Initially the bond strength is low because of higher percentage of hydroxyl component that



BOND STRENGTH WITH VARIATION OF BASE TO HARDNER RATIO

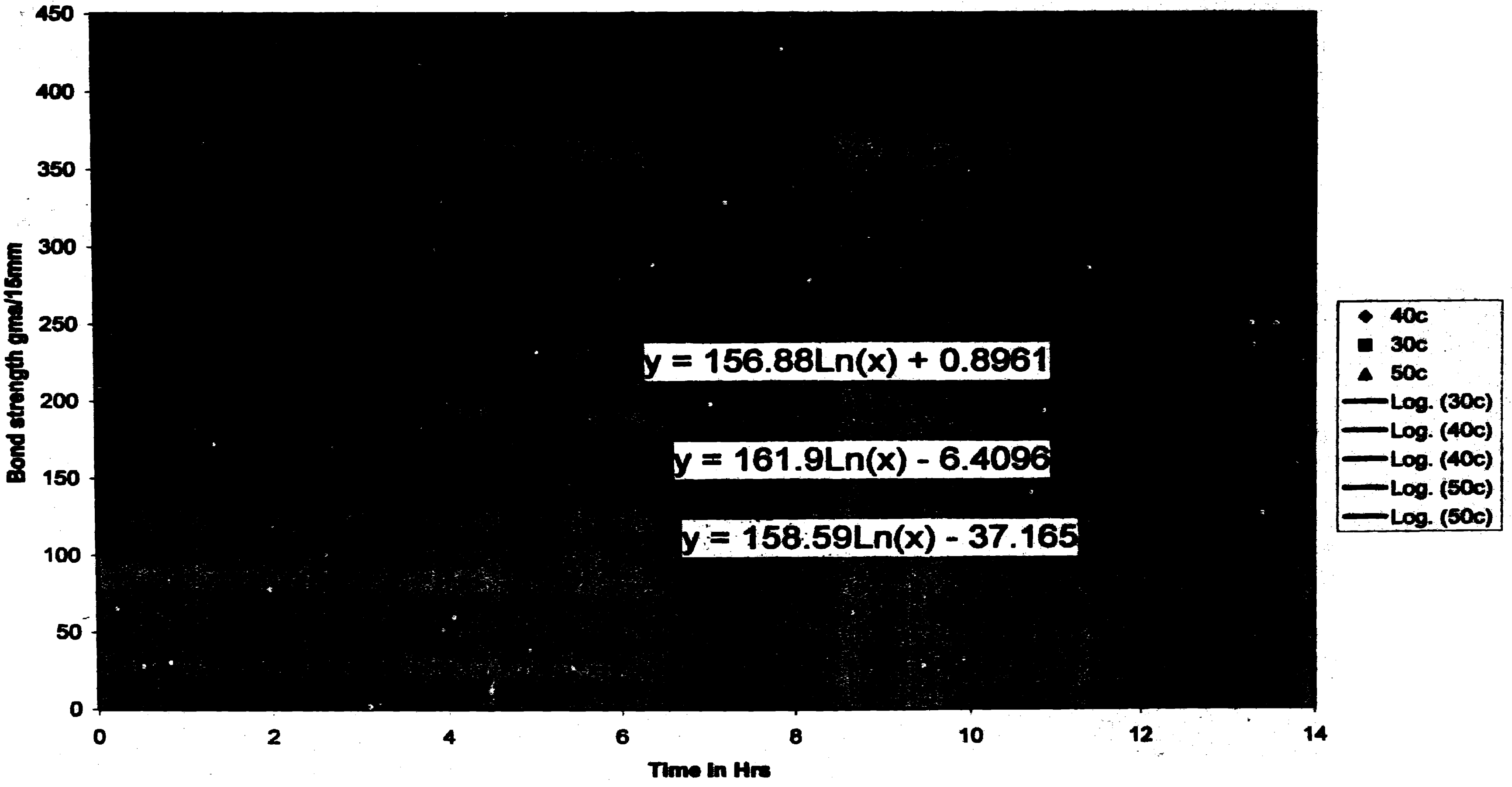
Fig. 12

remained unreacted .While with time, as the rate of reaction increases, the bond strength increases.

3.1.11 Effect of Time & Temperature on Development of Bond Strength

Fig. 13 presents the variation of bond strength of laminate with time and temperature. It may be seen from the figure that the bond strength increases from 100 gms/15mm to 400 gms/15mm in 12 hrs. The Kinetics of increase of bond strength follows an exponential equation .This suggests that the initial increase in bond strength is quite rapid followed by a decrease.

As the temperature of lamination increases the Kinetics of increase in bond strength with time increases. It seems that 40 C is the optimum temperature at which the laminate attains a reasonably saturated level of Kinetics of variation of bond strength with time. The high kinetics of initial increase in the bond strength at any temperature may be attributed to large availability and easy initial approach of hydroxyl and Isocyanate reactants for Urethane formation. The subsequent decrease is mainly due to vice-versa reasons, an increase in temperature of lamination increases the kinetics of activation of the monomer but the relative increase in the mobility of monomer may not be sufficient for urethane bond formation. A optimum balance of activation of monomer and mobility (approach of reactant for urethane formation) may be at 40 C. The conclusion is based on fact that at 50 C lamination, the kinetics varies little than that 40 C.



Bond strength withTime

Fig. 13

CHAPTER -4

4.0 Conclusion

The synthesized materials are comparable to the material that are used in the International market and the properties of the materials are suitable for commercial use of the material.

Annexure 1. Present the properties of two component solventless polyurethane adhesive available in International Market.

It may be seen that the viscosity of Isocyanate component varies from 1700 to 8000 mPa with specific gravity in the range of 1.1 to 1.2. The mixing ratio of the Isocyanate component with the Hydroxyl component varies from product to product. Generally, this is in the range of 100: 40 to 100: 70. The dynamic pot life of the mixture is 30 minutes at room temperature .The hydroxyl component is low in viscosity. Its viscosity varies from 400 to 2000 and specific gravity is nearly 1.0. The hydroxyl component mixed with NCO component in a Jet mixing pot and is pour on the roller directly. The roller picks up the adhesive and transfers it to the primary web. The primary web is then covered with secondary web.

Generally, the primary web is Polyester, Polyamide or PVC and secondary web is polyethylene, polypropylene, Ethylene propylene diene monomer etc. However there is no specific requirement identified.

The green bond strength of all solventless adhesive based laminate is vary low, with time, the bond strength increases and attain the further processable strength in 8 hrs. The bond strength generally varies with composition of the laminate. The property is between 120-350 gms/15mm (depending on the structure of the laminate and gsm of the adhesive coated). It is observed that the bond strength increases with the gsm of adhesive coated and finally become constant. But there are many other factors on which the bond strength depends, namely

- Nature of substrate to be laminated
- Type of the Ink
- Adhesive Composition and Mixing Ratio
- Surface Tension of the Films.
- Compatibility of adhesive with the substrates and Inks
- Thickness of Substrates and Processing Condition

Considering the entire factor except last, it was observed that Mor Free 406 A and C 83 (See Annexure-1) is the best adhesive composition followed by Mor Free 403 LV and C 83.

Primabond 85-96 A and Curative T-60 are similar to Mor Free 403 LV and C 83. This material shows following discrepancy.

- High Curing time
- Foaming/ Misting Formation
- Low peel bond strength
- Characteristic smell

Henkel Liofol UR 7732-22 and Hardner UR 6084-23 is better in this charecteristics from Primabond but is associated with following weakness in comperison to Mor Free 406 A and C 83

- Weak Bond strength

Duroflex 988 and C 88 camparable give higher bond strength than Henkel but lower than Mor Free 406 A and C 83 and is further associated with problem of speckling.

2K-LF 500 A and Hardener 424 of Herberts is worse than duroflex 988 and C 88 in terms of performance as follows.

- Characteristic smell
- Low peel bond Strength
- Higher curing time
- Speckling problem

Thus, in International level, 406A and C 83 appears to be the best commercially available flexible lamination two components adhesive. There are two national companies which have commercially introduced its Solventless lamination adhesive by the trade name Tacobond TL-100 and T-100 and Fevithane 2H22 and Fevithane 2R11. These two materials have a charecteristic smell in the adhesive and the cured products. The former is further associated with a permanent tack problem.

The developed formulation is much better than nationally available adhesive. This material does not have any smell in the laminate or in the adhesive. The bond strength of developed material is comparable to any above

adhesive. The gsm requirement of this adhesive material in laminate is much lesser. This material has a pot life comparable with 406 A and C 83. This adhesive do not leave any tack in the laminates , however, the developed adhesive has a problem of print transfer in case of printed substrate and aluminum transfer in case of metallized substrate . This Lacuna may be due to the high bond strength developed in the film which is in direct contact with the adhesive. It appears that the bond between the adhesive and the substrate which in turn is in contact with the second substrate has the tendency to develop more strength and with draw some site of adhesion from the second substrate leaving the bond between second substrate and the first substrate lesser than the bond between the adhesive and the first substrate.

ANNEXURE-1

DATA SHEET

MORTON ADHESIVE AND CHEMICAL SPECIALITIES

(1)Mor-Free 406 A + C 83 is a solventless 2 - component polyurethane adhesive system.

Product data	406 A NCO-Component	C 83 OH-Component
Solid Content (%)	100	100
Viscosity (mPass/25 C)	3000(2000-4000)	2000(1500-2500)
Specific gravity (g/cm3)	1.21	1.07
Mix ratio gravimetric		
Standard	100	45
For PA/PE	100	50
For Metallized films	100	35

(2) Mor-Free XVP 406 A LV + C 83 is a solventless 2 - component polyurethane adhesive system.

Product data	XVP 406 a LV NCO-Component	C 83 OH-Component
Solid Content (%)	100	100
Viscosity (mPass/25 C)	3000(2000-4000)	2000(1500-2500)
Specific gravity (g/cm3)	1.21	1.07
Mix ratio gravimetric		
Standard	100	60
For PA/PE	100	70
For Metallized films	100	50

4) Mor-Free VP 406 A LV + C 83 is a solventless 2 - component polyurethane adhesive system.

Product data	VP 406 A LV NCO-Component	C 83 OH-Component
Solid Content (%)	100	100
Viscosity (mPass/25 C)	3000(2000-4000)	2000(1500-2500)
Specific gravity (g/cm3)	1.21	1.07
Mix ratio gravimetric		
Standard	100	60
For PA/PE	100	70
For Metallized films	100	50

(4) Mor-Free 403 LV + C 83 is a solventless 2 - component polyurethane adhesive system.

Product data	403 LV NCO-Component	C 83 OH-Component
Solid Content (%)	100	100
Viscosity (mPass/25 C)	1700 +/- 400	2000 +/-500
Specific gravity (g/cm3)	1.17 +/- 0.02	1.07+/-0.02
Mix ratio gravimetric		
Standard	100	50
For PA/PE	100	60
For Metallized films	100	45

5) **Mor-Free** 403 LV + C-411 is a solventless 2 - component polyurethane adhesive system.

Product data	403 LV NCO-Component	C-411 OH-Component
Solid Content (%)	100	100
Viscosity (mPass/25 C)	1700 +/- 400	1100 +/-300
Specific gravity g/cm3)	1.17 +/- 0.02	1.10+/-0.02
Mix ratio gravimetric		
Standard	100	60
For PA/PE	100	70
For Metallized films	100	50

SOVEREIGN SPECIALTY CHEMICALS

Primabond 85-96 A + T 60 is a solventfree 2 - component reverse catalyzed polyurethane laminating adhesive system.

Product data	PRIMABOND 85-96A NCO-Component	CURATIVE T60 OH-Component
Solid Content (%)	100	100
Viscosity (mPass/25 C)	800-1400	400-700
Specific gravity g/cm3)	1.17	0.96
Mix ratio	100	70-90

ELCHEM ADHESIVE SPA

PURBINDER MP 755/ MP 850 is a solventfree 2 - component polyurethane adhesive system.

Product data	MP 850 NCO-Component	MP 755 OH-Component
Solid Content (%)	100	100
Viscosity (mPass/25 C)	approx.11000	Approx.5000
Specific gravity(g/cm3)	1.19	1.20
Mix ratio	100	70

HENKEL KGaA

LIOFOL UR 7732-22 / Hardener Ur 6084-23 is a solventfree 2 - component polyurethane adhesive system.

Product data	Liofol UR 7732-22 NCO-Component	Hardener UR 6084-23 OH-Component
Solid Content (%)	100	100
Viscosity (mPass) Sp. 27,	4500 +/- 1900 30 rpm, 40 C	3000+/-10000 30rpm, 20 C
Specific gravity g/cm3)	1.16	1.16
Mix ratio	100	40

NATIONAL STARCH & CHEMICAL A MEMBER OF ICI group

DUROFLEX 988 / C88 is a solventfree 2 - component polyurethane adhesive system.

Product data	988 NCO-Component	C 88 OH-Component
Solid Content (%)	100	100
Viscosity (mPass/25 C)	-	-
Specific gravity (g/cm3)	-	-
Mix ratio	100	45

HERBERTS ADHESIVE - COLOUR CHEM LTD.

HERBERTS - 2K-LF 500A / HARDENER 424 is a solventfree 2 - component polyurethane adhesive system.

Product data	HARDENER 424 NCO-Component	2K-LF 500A OH-Component
Solid Content (%)	100	100
Viscosity (mPass/25 C)	5000 +/-100	5000+/-1000
Specific gravity (g/cm3)	1.24	1.14
Mix ratio	100	60

TARAPUR COATING & ADHESIVE PVT. LTD.

TACOBOND TL-100 + T-100 is a solventfree 2 - component polyurethane adhesive system.

Product data	TACODUR T-100 NCO-Component	TACOBOND TL-100 OH-Component
Solid Content (%)	100	100
Viscosity (mPass/25 C)	5000-8000	1000-1500
Specific gravity (g/cm3)	-	-
Mix ratio	100	50

PIDILITE INDUSTRIES LTD.

FEVITHANE 2R11 + FEVITHANE 2H22 is a solventfree 2 - component polyurethane adhesive system.

Product data	FEVITHANE 2H22 NCO-Component	FEVITHANE 2R11 OH-Component
Solid Content (%)	100	100
Viscosity (Poise/30 C)	10-25	20-40
Specific gravity (g/cm3)	-	-
Mix ratio Standards	100	60
Metallized/Cellophane	100	55

ELCHEM ADHESIVE SPA.

ELOXENE LV 55 is a solventfree one- component polyurethane adhesive system.

Product data	ELOXENE LV 55 NCO-ended
Solid Content (%)	100
Viscosity (100 C mPa.s)	500+/-100
Specific gravity g/cm3)	1.09
NCO %	5.5

4.1 Future Scope

The present work is based on reverse two component flexible lamination adhesive technology. This technology is the most advanced technology available in this field. The material is based on indigenously available raw materials. The product is better than any indigenous developed technology and comparable to best available International product. Unfortunately this material is associated with a Lacuna of print / metal transfer as discussed above. This is probably due to the high bond strength of the adhesive .Therefore, a optimization of this product by reducing the bond strength is a pit hole to be fulfilled . This is the further scope of the technology which is to be investigation.

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